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EQ6, A Computer Program for Reaction-Path
Modeling of Aqueous Geochemical Systems:
User's Guide and Documentation

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PREFACE

This report on the EQ6 code is the third in a series on computer programs for use in modeling aqueous geochemical systems. EQ6 is a code for making calculations of thermodynamic or partial thermodynamic equilibrium in aqueous systems. It is normally used to compute reaction paths of dynamically reacting systems, in which equilibrium or partial equilibrium calculations are done at a sequence of steps of reaction progress and/or time. The code presently can integrate rate equations for mineral dissolution. Capabilities to handle the kinetics of other kinds of reactions are under development. The code is of general applicability in the field of aqueous geochemistry. However, the current development program is focused on providing calculational capabilities in support of performance assessment for geologic disposal of high-level nuclear waste.

EQ6 has been the subject of previous reports (Wolery, 1978, 1979). However, this report is the first user's guide written by the code's author. EQ6 is part of a software package called EQ3/6. The first report in this series (Wolery, 1983) is the user's guide and documentation for EQ3NR, the aqueous speciation-solubility code. EQ3NR calculations are required to initialize EQ6 computations. The EQ3NR document describes EQ3NR, the common data base that supports both EQ3NR and EQ6, and EQTL, a data base preprocessor code. The reader of this report should be fully familiar with the EQ3NR document.

The second report in this series (Wolery, 1984a) discusses modifications to EQ3NR and EQ6 to permit a choice of any of several sets of approximations for the activity of water and the molal activity coefficients of solutes, including options suitable for calculations on brines and concentrated salt solutions. These options have been built into the 3245 release package, of which the EQ6 described here is a part (See also Jackson, 1984). Wolery (1984a) describes the differences between the 3245 version of EQ3NR and the 3230 version described earlier by Wolery (1983).

The fourth report in this series (Wolery, 1984b) will be the user's guide and documentation for MCRT, a data base/temperature extrapolation code that supports the EQ3/6 thermodynamic data base. MCRT and its data files are now considered part of the EQ3/6 package.

Inquiries about obtaining the EQ3/6 package should be addressed to 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. Please note that no source codes or data files are reproduced in this report.

The documentation on EQ6 contained in this report exceeds what the user needs to know about it in order to run it. This is especially true concerning the descriptions of the numerical methods used in the code.

Those desiring to use EQ6 should become familiar with what the code can and can't do and how to format problems in the form of INPUT files. Examples of INPUTs and OUTPUTs should be especially helpful. Appendix D ("Running EQ6 and Related Codes at LLNL") may be useful. EQ6 is still under development with respect to adding new capabilities. The user should pay close attention to the version identification of the EQ6 he/she is using.

This report was written to correspond to the following code and data base versions from the package version EQ3/6.3245:

EQ3NR.3245U__
EQTL 3245U__
EQ6.3245U__

Appendix C briefly discusses the scheme used to identify versions of the EQ3/6 software package and the codes, and data files that are in it. It also summarizes the past history of EQ3/6 releases.

The sample problems in this report were run with data from the file DATA0.3175 (also designated as DEQPAK9 under an old identification scheme). The internal documentation of this version is largely incomplete. A DATA0.3245-series data base, now in preparation, will contain updated data with full internal documentation.

Comments from code users are welcome. Response to user comments on codes and data bases will be facilitated by inclusion of version identification.

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GLOSSARY OF SYMBOLS

- a (a) Thermodynamic activity; (b) superscript denoting an activity based function (e.g., ξ_1^a).
- A Thermodynamic affinity.
- Ah Thermodynamic affinity (per electron) of a redox couple with respect to the standard hydrogen electrode; $Ah = F E_h$.
- A_t Titration alkalinity, equivalents per kilogram of water; normally defined by the ph 4.5 - methyl orange - end-point.
- 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.
- $b_{i, \text{scale}}$ Affinity scaling factor defined by equation 7-97.
- c Stoichiometric mass coefficient; e.g., c_{rs} is the number of moles of element r per mole of aqueous species s .
- d Subscript denoting a dissolution reaction; e.g., A_d , the affinity to dissolve.
- $d\xi_i/dE$ Relative rate of the i -th irreversible reaction.
- $d\xi_i/dt$ Actual rate of the i -th irreversible reaction.
- $dt/d\xi$ Inverse rate of the overall irreversible reaction.
- d An array of derivatives of increasing order.
- D An element of the matrix D.
- D A matrix used to convert an array of finite differences of increasing order to an equivalent array of derivatives.
- e^- Electron; in the commonly practiced thermodynamic formalism, this is a hypothetical aqueous species, not a real one; though real aqueous electrons may actually exist, most notably in a gamma radiation field, their thermodynamic properties are not identical to those of the hypothetical aqueous electron.

- Eh Theoretical equilibrium electrical potential of a redox couple;
- $$Eh = \frac{2.303 RT}{4 F} (\log f_{O_2} - 4 pH - 2 \log a_{H_2O} - \log K_{Eh}),$$
- where f_{O_2} is understood to be the hypothetical equilibrium oxygen fugacity in aqueous solution.
- f (a) Fugacity; (b) superscript denoting a fugacity based function (e.g., $\lambda_{S_B}^f$); (c) a finite difference function; (d) ratio of effective to total surface area of a mineral.
- 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
- \underline{f} An array of finite differences of increasing order.
- F The Faraday constant, 23062.3 cal/equiv-volt.
- g Subscript indexing a gas species.
- h Hydration number of an aqueous species.
- H_{sr}^n The factor $n_s u_s / b_s r$.
- H_{zr}^n The factor $n_s z_s / b_s r$.
- H_{Ir}^m The factor $m_s z_s^2 / 2 b_s r$.
- H_{IEr}^m The factor $m_s u_s s_E / b_s r$.
- I Ionic strength.
- I_E Equivalent stoichiometric ionic strength of a sodium chloride solution; defined equivalent to the total molal concentration of either Na^+ or Cl^- , otherwise defined as zero.
- IAP Ion activity product; see Q.
- J An element of the Jacobian matrix.
- \underline{J} The Jacobian matrix ($\partial \alpha_i / \partial z_j$) used in Newton-Raphson iteration.
- k Rate constant for an irreversible reaction.
- K Thermodynamic equilibrium constant.
- K_{Eh} thermodynamic equilibrium constant for the half-reaction
- $$2 H_2O(l) = O_2(g) + 4 H^+ + 4 e^-$$
- K_w Equilibrium constant for the reaction $H_2O(l) = H^+ + OH^-$.

L_r	The quantity $\sum_{s=2}^{s_Q} b_{sr} \Gamma_s I$.
λ_1^a	Log a_w .
λ_{sB}^f	Log f_{O_2} .
λ_s^m	Log m_s .
λ_s^n	Log n_s .
λ_s^Y	Log γ_s .
λ_{IE}	Log I_E .
λ_I	Log I .
m	(a) Molal concentration; (b) superscript denoting a molality based function (e.g. λ_s^m).
n	(a) Mass of a species, in moles; (b) superscript denoting a mass based function (e.g., λ_s^n); (c) an exponent appearing in equation 3-34 or 3-35.
n^T	Total mass of a component, in moles.
$O_2(g)$	Oxygen gas; in aqueous solution, this refers to a <u>hypothetical</u> species similar to e^- ; also symbolized as O_2 .
p	(a) Subscript denoting a precipitation reaction; e.g., A_p , the affinity to precipitate; (b) coefficients appearing in equation 7-4.
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 used by many others to mean the same thing (e.g., Parkhurst et al., 1980).
r	Subscript indexing an aqueous reaction.
r_i	Short for the relative rate of the i -th irreversible reaction, $d\xi_i / d\xi$.
r_t	Short for the inverse rate of the overall reaction, $dt / d\xi$.
r_T	Total number of aqueous reactions.
R	The gas constant, 1.98726 cal/mol-°K.

- s (a) Subscript indexing an aqueous species ($s=1$ implies $H_2O(1)$);
 (b) surface area of a mineral.
- s' Subscript implying s in the range from 2 to s_Q , excluding s_B .
- s'' Subscript implying the species formally associated with the aqueous reaction designated by r ($s'' = r + s_B$).
- s_B Subscript denoting the hypothetical aqueous species $O_2(g)$.
- s_E Subscript denoting the master aqueous species (either Na^+ or Cl^-) that defines I_E .
- 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.
- SI Saturation index for a mineral; $SI = \log(Q/K)$, where Q and K are the activity product and equilibrium constant, respectively, for the dissolution reaction.
- t Time.
- t_0 Time parameter appearing in equation 3-36.
- T Temperature $^{\circ}K$.
- T_0 Temperature parameter appearing in equation 3-37.
- u Stoichiometric coefficient calculated from the stoichiometric reaction coefficients and certain model constraints;
 $u_{s',s}$ 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 Subscript denoting water (e.g., a_w , the activity of water);
 (b) weighting factors, as in equation 7-17.
- x (a) Mole fraction; (b) a general algebraic variable.
- z (a) Electrical charge; (b) a master iteration variable, an element of the vector \underline{z} ; (c) subscript or superscript implying a relation to the concept of charge balance (e.g., H_{zr} , $\alpha_{s_B}^z$).
- \underline{z} Vector of master algebraic variables for Newton-Raphson iteration.
- 2.303 Symbol for and approximation to $\ln 10$.

$\underline{\alpha}$	Newton-Raphson residual function vector.
α_1^a	Residual function for the activity of water.
$\alpha_{S_B}^z$	Residual function for charge balance.
α_S^n	Residual function for mass balance.
α_S^Y	Residual function for a molal activity coefficient.
α_{I_E}	Residual function for the equivalent stoichiometric ionic strength.
α_I	Residual function for the ionic strength.
α_ϕ	Residual function for equilibrium with a pure mineral.
$\alpha_{\sigma\psi}$	Residual function for equilibrium with a component of a solid solution.
$\underline{\beta}$	Newton-Raphson residual function vector, identical to $\underline{\alpha}$, except that mass balance residual elements are normalized.
β_{\max}	The largest absolute value of any element of $\underline{\beta}$.
δ	Newton-Raphson correction term vector.
δ_{\max}	The largest absolute value of any element of δ .
δ_{func}	Convergence function defined by equation 7-5.
δ'	Under-relaxation parameter appearing in equation 7-7.
Δ_1	Object function defined by equation 7-97.
$\Delta\xi$	Increment of reaction progress.
$\Delta\xi_i$	Increment of reaction progress for an individual irreversible reaction.
Δt	Increment of time.
$\Delta(\text{zn})$	Calculated charge imbalance.
γ	(a) Activity coefficient of an aqueous species; (b) superscript denoting an activity coefficient based function (e.g., γ_S^Y).
Γ_{1I_E}	$d \log a_w / d \log I_E$.
Γ_{1I}	$d \log a_w / d \log I$.
Γ_{1s}	$d \log a_w / d \log m_s$, for $s = 2, s_T$.
Γ_{sI}	$d \log \gamma_s / d \log I$, for $s = 2, s_T$.
Γ_{ss^*}	$d \log \gamma_s / d \log m_{s^*}$, for $s = 2, s_T, s^* = 2, s_T$.

$\underline{\delta}$	Newton-Raphson correction term vector.
δ_{\max}	The largest absolute value of any element of $\underline{\delta}$.
δ_{conv}	Newton-Raphson convergence function.
ϵ	Subscript indexing a chemical element.
ϵ_T	Total number of chemical elements in a chemical system.
ξ	Overall reaction progress variable.
ξ_i	Reaction progress variable for the i-th irreversible reaction.
κ	Under-relaxation parameter in Newton-Raphson iteration.
λ	Activity coefficient of a solid solution component.
Λ_{ij}	$d \log \lambda_i / d \log x_j$.
ρ	Specified values for relative rate derivatives (See equation 3-33).
σ	(a) Subscript indexing a component of a solid solution; (b) stoichiometric adjustment factor appearing in equation 3-34.
$\sigma_{T,\psi}$	Total number of end-members in a solid solution.
Σ_{hm}	The mass of water bound to solute species per kilogram of solvent.
φ	(a) Subscript indexing a mineral of fixed composition; (b) the osmotic coefficient of the aqueous solution.
φ_E	Total number of minerals of fixed composition in equilibrium with the aqueous phase.
ψ	Subscript indexing a solid solution.
ψ_E	Total number of solid solutions in equilibrium with the aqueous phase.
ω	water constant; $1000 \div$ molecular weight of H_2O , $\omega = 55.51$.
$+$	Subscript denoting a reaction proceeding in the forward sense; the convention in this report equates this with dissociation, dissolution, or destruction of the associated species.
$-$	Subscript denoting a reaction proceeding in the backward sense; the convention in this report equates this with association, precipitation, or formation of the associated species.

EQ6
A COMPUTER PROGRAM FOR REACTION-PATH
MODELING OF AQUEOUS GEOCHEMICAL SYSTEMS:
USER'S GUIDE AND DOCUMENTATION

ABSTRACT

EQ6 is FORTRAN computer program in the EQ3/6 software package. It calculates reaction paths (chemical evolution) in reacting systems consisting of water and other substances. Speciation in aqueous solution is an integral part of these calculations. EQ6 can compute models of titration processes (including fluid mixing), irreversible reaction in closed systems, irreversible reaction in some simple kinds of open systems, and heating or cooling processes, as well as solve "single-point" thermodynamic equilibrium problems. The code is being developed to make calculations in support of performance assessment of geologic disposal of high-level nuclear waste, but has very wide-ranging applicability in the field of aqueous geochemistry.

Conceptually, a reaction path consists of a sequence of thermodynamic equilibrium problems. Chemical evolution is driven by a set of irreversible reactions (i.e., reactions out of equilibrium) and/or changes in temperature/pressure. These irreversible reactions most often represent the dissolution of minerals or other solids. The code computes the appearance and disappearance of phases in solubility equilibrium with the water. It finds the identities of these phases automatically. The user may specify which potential such phases are allowed to form and which are not. If a phase is not permitted to precipitate according to solubility equilibrium, the aqueous solution may become supersaturated.

The code accepts two kinds of rate laws for irreversible reactions. One type gives only a relative rate ($d\xi_i/d\xi$), the rate of reaction progress of a reaction with respect to an overall progress variable. The other gives a

rate with respect to time ($d\xi_i/dt$). If all irreversible rates specified are relative, then the code operates in mode (called "arbitrary kinetics") which has no time variable. The code calculations are tied to a time frame if at least one of the rate laws describes an absolute rate.

EQ6 reads two secondary supporting data files (DATA2 and DATA3) that are created from a primary data file (DATA0) by EQTL, a data base preprocessor. The temperature range of the thermodynamic data on the data file is 0-300°C. Addition or deletion of species or changes in associated thermodynamic data are made by changing only the data file, not the code. The user can specify modification or substitution of equilibrium constants at run time by using options on the INPUT file.

EQ6 and the other codes in the EQ3/6 package were developed for the FTN and CFT FORTRAN languages on the CDC 7600 and Cray-1 computers, respectively. Special FORTRAN conventions have been followed to maximize ease of portability to IBM, UNIVAC, and VAX computers.

1. INTRODUCTION

1.1. EQ6 AND THE EQ3/6 PACKAGE

EQ6 is a FORTRAN program for making thermodynamic, reaction path, and kinetic reaction path calculations. It is part of the EQ3/6 package (Wolery, 1979). EQ6 computations must be initialized by speciation-solubility calculations done by its companion code, EQ3NR (Wolery, 1983). EQ3NR recently replaced the older and less efficient EQ3. EQ3NR calculates the distribution of aqueous species (simple ions, ion-pairs, and aqueous complexes). The computed aqueous phase model is then written on a file called PICKUP, which can be included in the EQ6 INPUT file. The user can then employ EQ6 to calculate models of titration processes, rock/water interactions, interactions of the water with substances other than rocks and minerals, effects of heating or cooling, fluid mixing, and so forth.

Calculations of this kind are useful in many areas in the field of aqueous geochemistry, as will be noted by the variety of examples cited in this report. The current development of EQ6 (and the rest of the EQ3/6 package) is focused on building calculational capabilities that will be used to support performance assessment of the disposal of high-level nuclear waste in geologic media. The waste disposal problem poses stiff problems in the realm of geochemical calculations. In particular, it will be necessary to develop reliable models for the interaction of ground water with rock and other substances found in and about the repository in order to assess the controls on the concentrations of dissolved radionuclides over significant periods of time. EQ6 is still under development to increase the scope of its capabilities to help meet these needs.

The relationship of EQ6 to the rest of the EQ3/6 package is shown in Figure 1. EQLIB is a subroutine library that supports all of the EQ3/6 codes. DATA0 is the common data base shared by EQ3NR and EQ6. It covers the temperature range 0-300°C, with corresponding pressures of 1.013 bar

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to see relation of EQLIB, etc

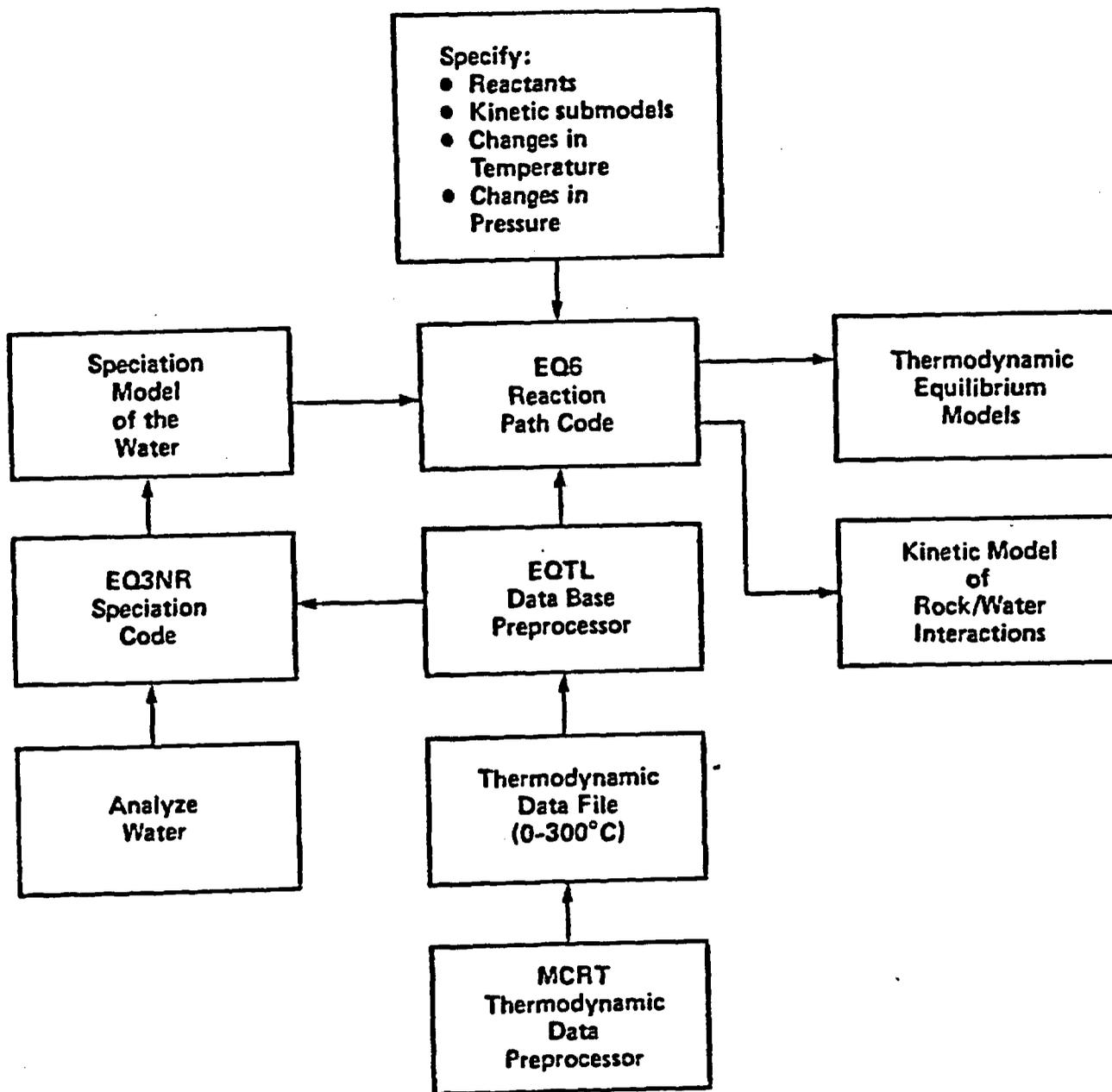


Figure. 1. The flow of information among the computer codes EQ3NR, EQ6, MCRT, and EQTL (After Wolery, 1983).

(1 atm) up to 100°C, and the steam/water equilibrium pressure at higher temperatures. Neither code reads DATA0 directly. Rather, a data base preprocessor, EQTL, writes a file called DATA1 for EQ3NR to read, and two files, DATA2 and DATA3, for EQ6. EQTL and the format of the DATA0 file are described by Wolery (1983) in the EQ3NR user's guide.

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MCRT (Wolery, 1984b) is a thermodynamic data base processing code that can be used to expand and revise the DATA0 file. It in turn has its own data files. It is one of the twin pillars of the EQ3/6 data base. The other is the SUPCRT data base of H.C. Helgeson and his colleagues (Helgeson et al., 1978; Helgeson and Kirkham, 1974ab, 1976; Helgeson et al., 1981) SUPCRT updates are issued periodically by Harold Helgeson's laboratory in Berkeley.

Both EQ6 and its supporting thermodynamic data base are extensively documented internally. They and the INPUT and OUTPUT files are designed to be transparent to users, as they are in the case of EQ3NR (Wolery, 1983). Users deal with chemical elements and aqueous, mineral, and gas species by names, not index numbers. The EQ6 OUTPUT file is self-documented. This can potentially be quite large. The user can effectively control it by means of print option switches. A graphics postprocessing capability is currently under development at LLNL.

EQ6 normally writes its own PICKUP file, which is a complete EQ6 INPUT file. This makes up the code's restart capability. It also allows a run to be made in segments, which is often more convenient than making a single long run. This file is set up to permit continuation of the preceding run segment. It can be modified if the user wishes to change the direction of the reaction path at this point.

EQ6 and the other codes in the EQ3/6 package have been written and tested on CDC 7600 and Cray-1 computers. Special FORTRAN conventions have been followed to maximize ease of portability to IBM, UNIVAC, and VAX computers. These conventions are described by Wolery (1983). The EQ3/6 software is now self-contained. The only special library required to support the codes in it is the EQLIB library, which is included in the package.

This report describes the assumptions underlying the use of EQ6 and documents the mathematical derivations and the numerical techniques that are used by the code. The user should already be familiar with the assumptions underlying the EQ3NR code (Wolery, 1983), and how to use that code. Several examples of the usage of EQ6, including the full INPUT files and pertinent parts of the OUTPUT files, are presented and discussed. The current state of development of the code, and a general overview of plans for further development, are also presented.

1.2. INPUT TO EQ6 FROM EQ3NR

To describe the function of EQ6, we first briefly review the type of output from EQ3NR. This contains the aqueous species distribution (the 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 ($SI = \log Q_+/K_+$, where Q is the ion activity product, K the equilibrium constant, and the "+" subscript signifies the dissolution reaction) of minerals in the data base. EQ3NR estimates the thermodynamic state of each aqueous redox couple (expressing it as couple-specific values of E_h , p_e , equilibrium oxygen fugacity, or A_h (redox affinity; Wolery, 1983). Differences in the values of these functions define the degree of disequilibrium among any two aqueous redox couples (See Wolery, 1983).

The speciation results from EQ3NR are in terms of molal concentration. Hence all masses of species and components are relative to one kilogram of solvent water. Each master species, except $O_2(g)$, corresponds to a chemical element in some oxidation state. EQ3NR computes the mass totals for these components, assuming a mass of aqueous fluid containing one kilogram of solvent. It does this for all master species, including the solvent (H_2O), which corresponds to oxygen in the negative divalent state, and the aqueous hydrogen ion (H^+), which corresponds to positive monovalent hydrogen.

These mass totals, along with logarithmic mass parameters for the corresponding master species, are written by EQ3NR on its PICKUP file. This file is normally incorporated into the EQ6 INPUT file (using a text editor or file merge utility), where it then makes up the bottom half of the file. The information transferred to EQ6 via the EQ3NR PICKUP file is sufficient for EQ6 to recalculate the speciation model. This calculation is made to satisfy the mass totals (and the required equilibria and all other pertinent constraints). Although the problem is somewhat reformulated, the basic

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governing equations in an EQ6 thermodynamic calculation are essentially those described by Wolery (1983) for EQ3NR. The logarithmic mass parameters written on the PICKUP file are used only as starting estimates in an EQ6 thermodynamic calculation. If none of the governing constraints on the problem have been changed on the EQ6 INPUT file, the values carried over from EQ3NR represent a satisfactory "answer," at least prior to any mineral precipitation.

Occasionally the user will change some of the pertinent constraints in going from EQ3NR to EQ6. For example one could change the options for approximating the activity of water and the activity coefficients of the solute species. Or, one might change some of the equilibrium constants, using the options that are available at run time. Generally speaking, for these examples, it would be safer to go back and execute these changes in an EQ3NR run. However, a very useful change in constraints in going from EQ3NR to EQ6 is the "temperature jump." This occurs when the temperature at the start of an EQ6 run differs from that pertaining to the results written onto the PICKUP file. This is handy when using the code to calculate high-temperature properties, such as pH or mineral saturation indices in an autoclave, when one has the pH, etc., for quenched fluid samples.

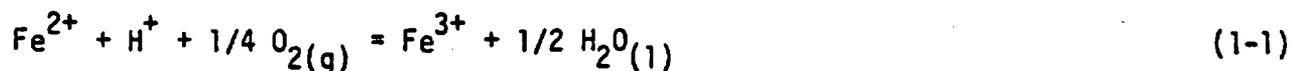
1.3. THERMODYNAMIC CALCULATIONS

EQ6 thermodynamic calculations differ from those performed by EQ3NR in two important ways. Recall that EQ3NR computes the speciation of an aqueous solution according to specified temperature/pressure, total concentrations of dissolved components, pH, Eh, and/or any other desired constraints (See Wolery, 1983). The first difference is that in EQ3NR the mass of solvent water is fixed at one kilogram, while in EQ6, this parameter is a variable to be calculated. The second is that EQ3NR calculations do not involve precipitating minerals, although EQ3NR can compute the concentrations of components that are required to satisfy desired heterogeneous equilibria. To make thermodynamic calculations in which supersaturated minerals are precipitated, the user of the EQ3/6 package must use EQ6.

EQ6 solves a more classical kind of thermodynamic equilibrium problem in which the total masses of master components are specified, along with the temperature and pressure, the reactions that are constrained by equilibrium, the equilibrium constants, and the equations describing thermodynamic non-ideality (i.e., activity coefficients). EQ6 always has one more mass balance to deal with than the corresponding EQ3NR problem, because the mass of solvent water is an additional unknown. Water is produced and consumed by a variety of chemical reactions. In most EQ6 calculations, even those involving mass transfer and reaction path models, the mass of water deviates very little from the initial value (ordinarily 1 kg or = 55.51 moles). It is likely differ significantly only in calculations that simulate fluid mixing or evaporation processes.

Some
Missing

The significance of including the oxygen mass balance and treating the mass of solvent as an unknown is not just that the solvent mass needs to be known precisely. Rather, it is that including this relation (or some equivalent relation) in the model is necessary in order to treat both pH and Eh (or any other redox function- EQ6 uses oxygen fugacity as the primary redox variable instead of Eh) as unknowns to be calculated in the thermodynamic calculation. Otherwise, the value of one of these parameters must be provided as an input to the calculation. Water, pH, and the redox parameter are linked together by redox reactions, such as the oxidation of dissolved ferrous iron:



These reactions have often trivial effects on the solvent mass, but the effects on pH and the redox parameter may be considerable.

An explicit electrical balance constraint is automatically included in the calculation if it is needed. This need depends on the presence of any redox reactions in the model. Otherwise, electrical balance is implicit in the mass balance relations. The data base includes the following two redox reactions:



These reactions form part of the calculated thermodynamic model unless they are specifically suppressed. Thus, the explicit electrical balance constraint normally appears in the calculations.

The older versions of EQ6 (Wolery, 1979) required the user to provide an electrically balanced input from EQ3NR (or its predecessor, EQ3; see Wolery, 1979). Now, however, ²Now EQ3NR writes the computed electrical imbalance on its PICKUP file, and EQ6 maintains this constant imbalance in its thermodynamic calculations.

At the present time, EQ6 carries mass balances for master species corresponding to only one redox state per chemical element. EQ3NR allows for separate mass balances for different redox states (for example, one mass balance for Fe^{2+} and another for Fe^{3+}), and can thus compute redox disequilibrium models (Wolery, 1983). Current planning calls for extending this capability to EQ6. However, the present EQ6 is restricted to computing models with overall redox equilibrium. The calculations therefore correspond to the case of a single or "system" Eh. A redox disequilibrium model input from EQ3NR will therefore be "equilibrated" by the initial thermodynamic calculation in EQ6.

All minerals and other solids read into memory from the data base are potential precipitates. The user may disallow the precipitation of such phases in the thermodynamic calculations by using appropriate options on the INPUT file. If precipitation of a phase is suppressed by one of these options, then the aqueous solution is permitted to be supersaturated with it. This often corresponds better to reality than assuming that just any possible solubility equilibrium is actually a controlling factor. The INPUT file options for choosing precipitation suppression are highly flexible: it is easy to suppress specific individual phases, groups of phases composed of specified components, or the whole lot of them. In general, all precipitation should be suppressed when the user is using the code to calculate high-temperature properties (such as pH in an autoclave) from measurements on solution samples that have been quenched to room temperature.

A thermodynamic calculation requires the pre-specification of the phase assemblage of the system for which the computation is made. This assemblage consists of just the aqueous phase in an unmodified PICKUP file written by EQ3NR. After making the thermodynamic calculation for such an assemblage, EQ6 checks to see if there are any non-suppressed phases for which the water is supersaturated. If there are any, then the code picks one to add to the phase assemblage and makes a new thermodynamic calculation. If this calculation is successful, it repeats the process as necessary to remove cases of supersaturation with respect to non-suppressed phases.

If the calculation does not converge, it usually means that the phase just added to the assemblage is incompatible with one that was already in it. In this case, the phase just added should replace the latter, rather than be added to it. The code automatically picks the phase to be deleted and begins a new thermodynamic calculation. This capability permits the code to recover if it picks what turns out to be the wrong phase to add to the assemblage.

The thermodynamic calculations made by EQ6 depend on the thermodynamic data that support the computations. These data are included on a supporting data file called DATA0, which is not read directly by either EQ3NR or EQ6. Addition or deletion of species, or changes in associated thermodynamic data are made on this file without any corresponding changes required in the EQ6NR or EQ6 source codes. After any changes are made to DATA0, the user should rerun the data base preprocessor to generate new versions of the data files that directly support EQ3NR and EQ6. Recall that EQ3NR reads DATA1, and EQ6 reads DATA2 and DATA3. If changes have been made that would alter the results of an EQ3NR calculation used to initialize EQ6, then that calculation should be repeated using the new version of DATA1.

It is possible to specify changes in the thermodynamic data at run time for both EQ3NR and EQ6. Changes specified on the EQ3NR INPUT file are written on the PICKUP file and hence automatically carried over to EQ6. It is not wise to specify any thermodynamic data modifications on the EQ6 INPUT file that would be inconsistent with the initializing EQ3NR calculation.

EQ6 uses a highly efficient modified Newton-Raphson algorithm to make its thermodynamic calculations (Wolery, 1979). This is similar to that which was recently incorporated into EQ3NR (Wolery, 1983). The equations for ionic strength functions and electrical balance are solved simultaneously with those describing mass balance and mass action (equilibrium, both homogenous and heterogeneous). EQ6 follows any basis-switching that was established in the initializing EQ3NR calculation. Pre-iteration optimization and under-relaxation techniques are employed automatically to assist in getting convergence of the iterative calculation. If necessary, the code will scan the range of water stability to find a starting value of the oxygen fugacity that will lead to convergence. The code also does this automatically.

In practical usage, most "equilibrium" calculations the user is likely to make using EQ6 really represent cases of what is called "partial equilibrium." The code describes the chemical system of interest in a calculation by an array of simple reactions, each with relatively few components in it, and with reaction coefficients that are either integers or simple rational numbers. The concept of partial equilibrium is that some (usually most) such reactions are in a state of equilibrium, while others, usually few in number and representing heterogeneous processes such as mineral dissolution/precipitation, are not. Thus, partial equilibrium could be equally well referred to as partial disequilibrium.

"Thermodynamic" calculations can be modified in conceptually simple ways to deal with partial equilibrium. One type of partial equilibrium has already been discussed above, that which results when an aqueous solution is supersaturated with respect to some solid phase, but there is no precipitation of that phase. EQ6 can do this now, as noted earlier. Another example would be the case of aqueous redox disequilibrium, where the behavior of a dissolved element must be described by separate mass balances for two different oxidation states, instead of a single mass balance for both forms and a mass action equation describing equilibrium between the two forms. EQ6 does not yet have the capability to model redox disequilibrium.

1.4. REACTION PATHS

A reaction path represents the process by which a set of irreversible (meaning "not at equilibrium") reactions proceed to a state of thermodynamic equilibrium. This represents the "dynamic" aspect of partial equilibrium. Consider the interaction of K-feldspar (KAlSi_3O_8) placed in contact with distilled water. This water is undersaturated with this mineral, so there is a thermodynamic driving force for the K-feldspar to dissolve.

The process can be divided into steps in which small increments of this mineral are added to the aqueous solution. This is equivalent to a titration process. The reaction path computation can be conceptualized as a sequence of thermodynamic equilibrium calculations for systems of increasing total masses of the potassium, aluminum, silicon, and oxygen components. The unreacted mass of the K-feldspar is not considered part of the system on which these calculations are made. This reaction path would terminate when there is no remaining mass of the reactant, or when the solution becomes saturated, whichever occurs first. If there is sufficient reactant present to saturate the solution, then part of the problem is to determine how much dissolution is required to achieve this condition. Along the path, various secondary minerals, such as gibbsite ($\text{Al}(\text{OH})_3$) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) may precipitate when their equilibrium solubilities are reached. Some, such as gibbsite, may be transient products, redissolving before the end of the reaction path. Determining which such minerals precipitate, when they precipitate, and if and when they redissolve, is also part of the problem.

Consider another simple scenario, which begins with an aqueous solution that is slightly undersaturated with respect to anhydrite (CaSO_4). The temperature is then increased in a sequence of steps from the initial value to some sufficiently high value to precipitate this mineral, which has retrograde solubility. At some intermediate temperature the solution will become saturated and the mineral will be precipitated in increasing amount as the temperature is raised further. This can also be conceptualized as a series of

thermodynamic calculations. Here, however, the total masses of the components remain constant, but the change in temperature changes the thermodynamic properties of the system. Part of the problem here is to find the temperature where precipitation begins, and to quantify the extent of precipitation as a function of temperature.

Reaction path problems can be defined with more than one irreversible reaction proceeding simultaneously. It is also possible to define such paths which include both irreversible reactions and changing temperature/pressure. These will be referred to collectively as "irreversible processes." The extent of such processes can be described by reaction progress variables (Helgeson, 1968). They are usually denoted by the Greek letter ξ (xi). Some physical feel for them can be introduced by pointing out that reaction paths are calculationally equivalent to titrations. The reaction progress variable is either equivalent or proportional to the quantity of titrant, or reactant, that has been consumed in the titration (along the reaction path). More rigorous definition of reaction progress variables will be deferred to the next chapter. When there is more than one irreversible process, each is described by its corresponding reaction progress variable (ξ_i). The evolution of the system as a whole can also be described by an overall reaction progress variable (ξ).

Reaction path calculations take place without reference to a time frame if the rate functions specified by the user for the irreversible processes are so-called "relative rates" that measure the extent of reaction with respect to an overall reaction progress variable. Time is completely arbitrary and the most that one can say is that time increases as reaction progress increases. Wolery (1979) dubbed this kind of modeling "arbitrary" kinetics. If the rate for one or more irreversible processes is an "actual" or "absolute" rate, which measures the extent of reaction with respect to time, then the calculations take place in a time frame. It is then possible to calculate both a relative and an actual rate for each irreversible process.

The major obstacle to kinetic reaction path modeling is getting the descriptions of the "actual" rates. For each irreversible process, the user

must provide both a rate law and the appropriate constants. The study of the kinetics of reaction occurring in aqueous geochemical systems is still very much in the pioneering stage. There is not much general agreement with regard to the functional form of the rate laws, let alone the values of the corresponding constants (rate constants, activation energies, etc.). The user must be prepared to justify whatever kinetic descriptions he or she chooses to employ. EQ6 is set up to offer a choice of rate law options, and more can be easily added by inserting appropriate coding into subroutine RTCALC. There is no supporting kinetic data file corresponding to DATA0, the thermodynamic data file. Constants required to evaluate rate laws are instead entered on the INPUT file.

There is a two-fold advantage of kinetic over non-kinetic reaction path calculations. The first is that the calculations can be related to a time frame. The second is that the ratio of the rates of any two simultaneous irreversible processes is realistically evaluated as the ratio of the two actual rates. In non-kinetic calculations, such a ratio is evaluated as the ratio of the corresponding relative rates, which must be somewhat arbitrarily chosen by the user and are generally constants throughout the run.

The extra price that must be paid in making kinetic calculations is that the code is faced with integrating ordinary differential equations (the rate laws). The number of steps along the reaction path, hence the number of thermodynamic calculations that must be made, must be sufficiently large to solve these equations with acceptable accuracy. In non-kinetic calculations, the step size can be made fairly large, which reduces the time and expense of the computation.

To define a reaction path problem to run on EQ6, the user supplies a thermodynamic model of an aqueous solution, obtained by running EQ3NR, chooses a set of irreversible reactions and/or changes in temperature pressure, inputs parameters to define the rates of these processes, and picks various options that are available. The code does the rest. It may be necessary to repeat a run several times, changing various options, before a model results that satisfactorily describes a given situation. Repeated runs may also be needed

to establish the sensitivity of the results to the assumptions that go into the calculations, for example the values of certain of the supporting thermodynamic data, the rate laws that were chosen, the kinetic parameters, etc.

2. MORE ABOUT EQ6

2.1. HISTORICAL DEVELOPMENT

H.C. Helgeson introduced the first computer program for making reaction path calculations in geochemical systems (Helgeson, 1968; Helgeson et al., 1970). It computed reaction path models along the lines of "arbitrary" kinetics. This code, called PATHI ("PATH-one"), performed its own initializing aqueous speciation-solubility calculation. Unlike EQ6, however, that was the only type of "single point" thermodynamic calculation the code could make. It had no capability to precipitate supersaturated phases at the start of a run, and consequently would terminate execution when supersaturation were encountered at this point.

The major difference between PATHI and EQ6 was that PATHI, once past the initializing calculation, treated all the equations governing the reaction path as ordinary differential equations, or ODEs as they are commonly referred to in the numerical methods literature. This was done by differentiating all the algebraic equations such as mass balance, mass action, etc., with respect to ξ , the overall progress variable, to put them in the same class with the relative rate expressions. Numerical integration of these equations gives results that, at the same points of reaction progress, and ignoring errors in the integration, would be equivalent to results obtained using EQ6.

The ODE integration method in PATHI was fairly simple. The first and second derivatives of the mass variables used to describe the model were evaluated after each step by solving a matrix equation similar to the Jacobian matrix used by EQ6 in performing Newton-Raphson iteration in the thermodynamic calculations. In fact, for the same choice of master variables, the matrices would be identical!* They are solved, however, for different right-hand-side

*EQ6 actually uses a different set than the one used by PATHI.

vectors. In the case of PATHI, solution with one right-hand-side gave an array of first-order derivatives, and solution with another gave the second derivatives. Making a step to another point of reaction progress was done by evaluating the second-order Taylor's series in which these derivatives appeared.

The method described above is a very inefficient way of integrating ODEs. Execution times of PATHI were extremely long. Nevertheless, the code was capable of making useful calculations, which demonstrated the utility and significance of such calculations. The code operated in one of two modes. The first simulated reaction in a closed system, in which the undissolved portions mineral reactants were considered to be in the system as a whole, but not in the "equilibrium" part. The second mode was a spin-off from the first, simulating reaction in a flow-through open system that focused on the evolution of a packet of aqueous solution flowing through a medium containing reactant minerals. The chief difference was that transient secondary minerals were considered to be left behind the moving packet of water, so that they could not alter its subsequent evolution by redissolution.

PATHI's calculational capabilities were demonstrated in some early modeling studies. Helgeson et al. (1969) applied it to a theoretical study of the weathering of feldspar and feldspathic rock and the evolution of the participating aqueous solutions. Helgeson (1970) also presented several examples of calculations pertaining to hydrothermal ore deposition.

The integration scheme used in PATHI was inefficient because as it moved to a new point of reaction progress, it made no use of the information at immediately preceding points. Essentially, doing so involves constructing finite difference functions up to orders as high as four to eight. Only the first derivatives then need be solved by the matrix equation noted above. The second and higher derivatives are then approximated by finite difference functions. This is what happens when one utilizes a method such as the predictor-corrector methods of variable order described by Gear (1971ab). This writer knows of at least two modifications of the PATHI code (both unpublished) that incorporated Gear's methodology. One was put together at

Los Alamos National Laboratory (C. Herrick, written communication, 1976). The other was the FASTPATH code (Schlitt and Jackson, 1981) developed at the Kennecott Copper Company.

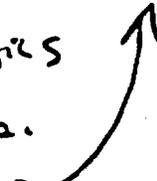
These "souped up" versions of Helgeson's original code were much more efficient, but they still had three drawbacks. One was the inability to deal with an initial aqueous solution with supersaturations. The second drawback was "drift," or manifestation of error in the integration along the reaction path. Perhaps of most concern was a developing calculated charge imbalance. This was periodically fixed by executing an aqueous speciation-solubility calculation (just like the initializing calculation) that readjusted the total concentration of one of the ionic components. The legitimacy of this procedure is dubious. A third drawback was that for many types of problems, the ODE integration methods are inherently less efficient than methods that use direct, independent thermodynamic calculations at given points of reaction progress. The step size limitations of the ODE method, based on the need to maintain accuracy, require that the calculations be performed at many intermediate points in order to get to a desired one.

EQ6 (Wolery, 1978, 1979) is in one sense a successor to Helgeson's original path code, in that it was written to perform the same modeling functions. It was, however, a completely new code. Separation of the solution of algebraic and differential equations eliminated both the problem of what to do with an initially supersaturated solution, and also the problem of "drift." The use of the Newton-Raphson method to solve the algebraic equations appearing in thermodynamic calculations was influenced by the paper of Morel and Morgan (1972), which introduced the equilibrium code REDEQL. EQ6 does use a finite-difference based method to generate predictor functions for the master variables. This is highly analogous to the predictor functions used in the Gear (1971ab) ODE integration method. However, EQ6 uses these results as starting estimates for the Newton-Raphson thermodynamic calculations. This replaced the corrector part of the ODE integration scheme. Upon making a step of reaction progress, EQ6 corrects to satisfy the governing algebraic equations, instead of their differential counterparts. Originally, EQ6 had no capability to deal with actual kinetics.

Wolery (1978) initially used EQ6 to model the interactions between sea water and basalt in hydrothermal systems at mid-ocean ridges. It was later applied to a study of rock/water interactions in a dilute-water geothermal system (Taylor et al., 1980) and to the dissolution of uranium dioxide in ground water at low and elevated temperatures. Brimhall (1980) used EQ6 to test a hypothesis for the origin of the copper ore body at Butte, Montana. EQ6 was also used by Janecky (1982) to model the hydrothermal interactions of oceanic peridotite with sea water. Garven (1982) used the code in a study of the role of ground water flow on the genesis of stratabound ore deposits. Kerrisk (1984) used EQ6 to make reaction-path calculations pertaining to the evolution of ground water and formation of secondary minerals at Rainier Mesa, Nevada. Isotopic calculations have been added to a branch version of EQ6 at the California Institute of Technology, and applied to geochemical modeling of sea water/oceanic crust interactions (Bowers and Taylor, 1983; Bowers et al., 1983).

The addition of kinetics to EQ6 was a more recent development. The kinetics capabilities of the LLNL version are described here for the first time. At present, the kinetics capability is limited to the treatment of mineral dissolution reactions. They have already been used in two early studies of the kinetics of hydrothermal interaction between devitrified tuff and ground water from the Nevada Test Site (Wolery and Delany, 1983; Knauss et al., 1983). A branch modification of EQ6 in H.C. Helgeson's laboratory at the University of California at Berkeley has a similar kinetics capability (Helgeson and Aagaard, 1979; Helgeson and Murphy, 1983a).

The development of kinetic reaction path modeling follows the recent growth of interest in geochemical kinetics beginning in the late 1970s. Much information has recently come to light pertaining to the nature of mechanisms and rate laws (See for example Aagaard and Helgeson, 1977, 1982; Berner, 1978, 1980, 1981b; Berner and Holdren, 1979; Dibble and Tiller, 1981; Holdren and Berner, 1979; Grandstaff, 1976, 1977, 1978; Helgeson and Murphy, 1983b, in press; Knauss and Wolery, 1984, in preparation; Lasaga, 1981ab; Murphy and Helgeson, 1983ab, in press; Petrovich et al., 1976; Petrovich, 1976, 1981ab; Rimstidt and Barnes, 1980; Schott et al., 1981; and Wood and Walther, 1983).

Kinetics
Refs. 

Kinetic reaction path modeling has only become a possibility due to the recent availability of quantitative descriptions of the rates of some geochemically important reactions. Much work remains to be done to establish a solid and widely applicable data base of rate laws and rate parameters.

From a computational standpoint, the inclusion of actual kinetics means that EQ6 must now face the problem of integrating ODEs (here, the rate laws relating reaction progress to time). At the present time, EQ6 calculates predictor functions for the rate functions, just as it does for the master variables. However, the usage is somewhat different in that the calculation is dependent on the predictor functions for the rates being accurate. The code uses these functions to integrate the rates to compute the increments of irreversible reaction (i.e., changes in the total masses of the components). In contrast, the predictor functions for the master variables do not have to be accurate, because correction is made by the Newton-Raphson thermodynamic calculation. Therefore, in a kinetic reaction path run the step sizes will generally be kept smaller than if there were no actual kinetics in the model, and the run will take longer to execute.

Another recent development in the evolution of EQ6 has been the addition of options to calculate the activity of water and the activity coefficients of aqueous solutes in concentrated solutions, such as natural brines (Wolery, 1984). EQ6 formerly offered only an equation due to Helgeson et al. (1970) for the activity of water and the B-dot equation of Helgeson (1969) for solute activity coefficients. This option has been preserved, but should not be used when the ionic strength exceeds about one molal. The major new option to date is the use of Pitzer's (1973) equations. However, the code has been modified to deal with any such equations that depend on the specific aqueous solution composition, not just the ionic strength. These new capabilities are limited by the available data base (See Wolery, 1984).

2.2. LIMITATIONS AND FUTURE DEVELOPMENT

The user of EQ6 should be aware of its limitations, both those that are inherent in any code of this type, and also those that pertain to the current state of development of the code. EQ6 is currently under development, and this process will continue for about another four years. Users should pay careful attention to the stage of development of the versions of EQ6 that they are using, because updated releases will be issued at six to twelve month intervals during this period.

What goes into a computer code is a strong determinant of what comes out of it. One such factor affecting EQ6 is the scope and quality of the thermodynamic data base. It is particularly important that all the species that should be significant contributors to the mass balances in the thermodynamic calculations be represented in the supporting thermodynamic data base, even if the corresponding data are not of high quality. It is not legitimate to leave an important species out of the model just because there are no good data for it. If necessary, perturbation calculations on the data in question should be done (using the NXMOD option feature) to get some handle on the sensitivity.

Similar comments pertain to other supporting data. If the user is modeling the behavior of brines, loosely defined here as any aqueous solutions with ionic strengths greater than one molal, then an appropriate activity coefficient option should be selected (See Wolery, 1984). In such cases, the user knows the limitations imposed by both the option itself and also those related to the scope and quality of the data base that supports the option. *

The area of kinetics (actual kinetics) poses some special problems. Here, growth of knowledge is now progressing at a fast pace. There are still a number of questions regarding rate laws themselves, let alone such supporting data as rate coefficients and activation energies. The user must bear the burden of assuring that he is using the correct rate laws and supporting

parameters. The EQ6 code is set up to treat rate laws in modular fashion. The currently programmed rate laws can be modified and new ones can be added. The user selects from among the programmed rate laws and provides the necessary supporting data on the INPUT file. There is no kinetic data file to parallel the thermodynamic data file.

Some of the important limitations on the use of EQ6 pertain to the exclusion or primitive level of development of important factors. Chief among these cases are:

1. No provision for sorption reactions (surface chemistry)
2. No provision for redox disequilibrium
3. The treatment of kinetics is restricted to dissolution reactions
4. The treatment of solid solutions is very limited
5. No pressure corrections for pressures off the one atmosphere-steam pressure curve

There are plans to address all of these deficiencies in the next couple of years of development.

The lack of provision for sorption reactions, here defined as restricted to chemical interactions on the surfaces of minerals and other solids, and the primitive treatment currently provided for solid solutions (which includes ion exchange in zeolites and smectites) may particularly limit the applicability of the current version of the code in predicting the behavior of many trace components. The development of specific models for sorption processes and for solid solution thermodynamics is presently in an active state of evolution. EQ6 will be set up to deal with these in a modular fashion similar to that employed in dealing with rate laws. In fact, it is likely that in future development, at least some of the rate laws for mineral dissolution and precipitation will be linked, as suggested by an example presented by Lasaga (1981a).

Redox disequilibrium is a factor that appears in many natural and artificial environments, and is important to recognize in geochemical modeling

(See Wolery, 1983, Chapter 2.3.5). It would be helpful to be able to model even simple redox disequilibrium, in which there is no interconversion of the forms of an element in more than one oxidation state. For example, Janecky (1982) found it necessary to modify a version of the EQ3/6 data base to "fool" EQ6 into treating sulfate and sulfide as separate components so that sulfate reduction was entirely suppressed. However, although this method (modifying the data base) does permit redox disequilibrium calculations to be made, it is not a satisfactory long-term solution to the problem.

The kinetics of redox and precipitation processes are also important factors in geochemical modeling. The need to include precipitation kinetics has already been apparent in attempts to model hydrothermal interactions experiments involving devitrified tuffs and a Nevada Test Site ground water (Wolery and Delany, 1983; Knauss et al., 1983). The kinetics of sorption processes may also be important in some settings.

One particular limitation of the existing thermodynamic data base is that there is no provision for making pressure corrections for cases in which the pressure does not lie on the the one atmosphere-steam pressure curve. There are plans to correct this deficiency in the near future.

It is important to recognize that the user is called upon to make important decisions at the start of the run. The code can at best provide workable defaults, meaning choices that allow the code to run. However, such choices may not be always suitable for the situation of interest. For example, unless the user specifies otherwise, the code will precipitate any mineral in the data base that supersaturates the aqueous solution. It may be more realistic in many cases to allow allow precipitation of only appropriately selected phases. Future code development will aggravate this situation by making more options to choose from. For example, once the precipitation kinetics capability is in place, the user will have to choose whether a potential secondary mineral will be (a) precipitated as required by solubility equilibrium, (b) not precipitated even if the fluid is supersaturated, or (c) precipitated when supersaturated, but according to precipitation kinetics instead of solubility.

2.3. OTHER CODES OF INTEREST

This introduction to EQ6 would not be complete without some mention of other codes that do the same or similar things. A complete and comprehensive discussion of such codes, comparing and contrasting their merits, is well beyond the scope of this report. Discussion here is limited to summarizing a few major alternative codes. For more general reviews, the reader is referred to Wolery (1979, 1983), Potter (1979), or Jenne (1981). The codes selected for discussion here have been used in geochemical applications, described in the scientific literature, and distributed in the scientific community by their originators. These are:

1. PATHI (Helgeson, 1968; Helgeson et al., 1970) and its derivatives
2. REDEQL (Morel and Morgan, 1972; McDuff and Morel, 1973)
3. MINEQL (Westall et al., 1976)
4. PHREEQE (Parkhurst et al., 1980; INTERA, 1983ac)
5. SOLVEQ/GEOCAL/MINSOLV/COOLBREW/CHILLER (Reed, 1977, 1982; and 1983, written communication)

If pressed to recommend an alternative to EQ3/6, the writer would suggest PHREEQE, then Reed's codes. The writer feels that PATHI and its derivatives have too many numerical disadvantages to recommend for continued use. The writer is also of the opinion that most of the extant versions of REDEQL and MINEQL are not suitable for general purpose reaction path modeling, although they are quite serviceable for a number of specific types of problems.

The original path program (PATHI) and two numerically "souped up" versions (the LANL and Kennecott modifications) have been discussed in the previous section. As noted earlier, these all relied on the conversion of governing algebraic equations to ordinary differential equations, followed by numerical integration. The less satisfactory aspects of this approach (no ability to precipitate supersaturated minerals from the initial aqueous solution, the "drift" problem) were also noted.

Nevertheless, it is worth noting that other PATHI-like codes exist. For example, there are the twin French codes DISSOL and EVAPOR, which were developed by Fritz (1975) to model dissolution and evaporation processes, respectively. He used them to model the weathering of granite. Al-Droubi (1976) and Al-Droubi et al. (1976, 1980) applied EVAPOR to problems concerning the effect of evaporation on the evolution of waters of the system of Lake Chad. Knight (1976) has written another code of the PATHI type, which he applied to the study of alunite and copper-arsenic sulfosalt deposits. This code was more recently used by Capuano and Cole (1982) in their study of the hydrothermal system at Roosevelt Hot Springs, Utah.

REDEQL (Morel and Morgan, 1972) is primarily a Newton-Raphson based speciation-solubility code. However, it also has some capacity to dissolve and precipitate minerals. There are two major derivatives of REDEQL, REDEQL2 (McDuff and Morel, 1973) and GEOCHEM (Mattigod and Sposito, 1979). Codes in the REDEQL series have been mainly used in environmental engineering studies (see for example Morel et al., 1973, 1976; Mattigod and Sposito, 1979).

MINEQL (Westall et al., 1976) is a daughter of REDEQL by virtue of an essentially similar approach and an overlap in co-authorship of the two codes centering on Francois Morel. MINEQL is a smaller code than REDEQL, is very popular among environmental engineers and sorption chemists, and forms a line of codes in its own right. There are a large number of customized versions of this code at various institutions. MINEQL is used quite extensively as a medium for testing various models of sorption processes that can not be evaluated without the presence of an aqueous speciation model. Nordstrom et al. (1978) give references to a fair number of studies of this kind.

It is somewhat dangerous to make sweeping generalizations about the characteristics of REDEQLs and MINEQLs because of the large numbers of customized versions. Nevertheless, having made this caveat, the writer will proceed. Most of the versions of these codes are not really set up to be full-scale reaction path programs. That is one reason why the writer does not recommend using these codes as such.

However, there is a more serious problem with most of the extant versions. That is that they do not provide a complete treatment with regard to balances for electrical charge and the components H_2O and H^+ (See the discussion by Reed, 1982). They simply ignore production or destruction of water along a reaction path. The two balance equations for electrical charge and the H^+ component are replaced by a single equation, the so-called "proton" condition of Morel and Morgan (1972). The proton condition can be viewed as a reduced form of either the charge balance equation or a mass balance equation for the H^+ component. This equivalence is not exact if the solvent mass is not fixed.

Even ignoring possible changes in solvent mass, which are most often negligible in terms of the effect on concentrations, the problem remains that two equations have been replaced by only one, hence one corresponding unknown must be treated as an input parameter. The effect is that mainstream versions of these codes can not compute both pH and Eh as unknowns, but have to be told the value of one or the other. This problem appears to have been overcome in the derivative of MINEQL called MINTEQ (Felmy et al., 1983, draft report cited by Peterson et al., 1983). This was apparently accomplished by including an extra balance equation representing a component in a second oxidation state. The writer is not aware of whether or not MINTEQ calculates changes in the mass of solvent.

PHREEQE (Parkhurst et al., 1980) is both a speciation-solubility and a reaction path code. PHREEQE uses a combination of numerical methods: a so-called "continued fraction" approach (See Parkhurst et al., 1980) and a modified Newton-Raphson method. It was not designed as a full-blown reaction-path code. This is most evident in the high extent of user interaction that is required to use the code in this mode. The runs must be made in segments that go up to, but do not cross, phase boundaries. There are both good and bad aspects of this. On the positive side, the relatively high degree of interaction tends to force the user to understand what is going on in the calculations. In this sense, PHREEQE is an excellent training vehicle. On the negative side, such a level of interaction may become monotonous, and the demand on the user's time becomes harder to justify.

A important caveat about PHREEQE is that it does not calculate changes in the mass of solvent (Parkhurst et al., 1980, p. 47-48). On the other hand, PHREEQE can calculate both pH and Eh as output variables, thanks to the use of a charge balance equation and an electron balance equation. The latter is a unique development due to Don Thorstenson, one of the authors of PHREEQE.

PHREEQE was written in part to replace an earlier code called MIX2 (Plummer et al., 1975). It was restricted to dealing with calculations for the system $\text{CaO-MgO-Na}_2\text{O-K}_2\text{O-CO}_2\text{-H}_2\text{SO}_4\text{-HCl-H}_2\text{O}$, was "hard-coded" for these specific components, and hence was not as generally applicable as PHREEQE. PHREEQE and MIX2 have primarily been used in studies of ground water evolution in carbonate terrains. An excellent discussion of the modeling concepts, illustrated with specific examples, and summarizing much previous work using these codes, is given by Plummer et al. (1983). The writer enthusiastically recommends reading this paper to anyone who is interested in reaction path modeling.

PHREEQE was examined for its suitability to applications in nuclear waste disposal performance assessment by INTERA (1983a). EQ3/6 was also chosen for this purpose (INTERA, 1983b). These reports constituted user's manuals for these codes. The former is an extension of the report by Parkhurst et al. (1980). Some modifications were made to the code. This version was dubbed PHR1. The other report by INTERA constituted a user's manual for the 3015 release of EQ3/6 (the subject of the current report is the 3245 version of EQ6; the 3230 release came out in between the 3015 and the 3245).

PHREEQE and EQ6 were used in the only direct comparison verification study of two reaction path codes (INTERA, 1983c) known to the writer. The codes were modified allow the use of the same activity coefficients, and data base preprocessors were written to permit data base conversion. This study found that, when both codes used the same activity coefficient equations and the same thermodynamic data, the results were virtually identical. Three reaction path tests were carried out: dissolution of microcline in dilute HCl solution, reduction of an oxygenated aqueous solution in equilibrium with calcite and hematite by addition of methane, and carbonate aquifer dedolomitization by

gypsum solution with increasing temperature. The results of the second test were especially encouraging, because the problem posed stiff changes in the redox state of the system, which makes the problem more of a calculational challenge than usual, and the two codes use very different methods of handling the redox aspect of the calculations.

Another series of speciation-solubility and reaction path codes was developed by Reed (1977, 1982). Unfortunately, there are no user's manuals for these codes. Reed's reports to date concentrate on the underlying geochemical theory, the numerical aspects, and the presentation of examples of calculations. His codes use a Newton-Raphson method (as do REDEQL, MINEQL, PHREEQE, and EQ3NR and EQ6). According to Reed (1983, written communication), SOLVEQ and GEOCAL are used to make speciation-solubility calculations, MINSOLV does isothermal reaction path calculations, CHILLER makes calculations of heating and cooling effects, and COOLBREW calculates the effects of mixing hot and cold waters. In the EQ3/6 package, EQ3NR is functionally equivalent to SOLVEQ and GEOCAL, and EQ6 does the functions of MINSOLV, CHILLER, and COOLBREW.

Reed's (1977) Ph.D. thesis presents applications of his codes to modeling metasomatism and ore deposition in hydrothermal systems in submarine volcanic rocks. Reed (1982) presented two specific examples of the use of his codes. One calculation simulated the heating of sea water from 25 to 300°C. The other simulated the reaction of rhyolite with an aqueous solution at 250°C. These codes have also been used by others (Bischoff and Seyfried, 1978; Mottl et al., 1979; Seyfried and Dibble, 1980; and Seyfried and Bischoff, 1981) to calculate the pH at temperature in autoclaves from the pH measured at 25°C (quench pH). The same calculations also give the saturation indices of relevant minerals at the temperature of the experiments.

3. INPUT CONSTRAINTS, GOVERNING EQUATIONS, AND OUTPUTS

3.1. GENERAL DISCUSSION

As noted earlier, in EQ6 there is a separation in the methodology of treating equations that are intrinsically algebraic from those that are by their nature differential. The former govern the purely thermodynamic calculations, and the latter consist of rate laws for irreversible processes. This numerical decoupling makes it possible to perform thermodynamic calculations, given the necessary inputs of total masses of components, the temperature, and the pressure, independently of the integration of rate equations (unlike, for example, in the code PATHI; Helgeson, 1968, Helgeson, et al., 1970). In particular, this decoupling permits making "single point" thermodynamic calculations, such as the temperature jump, which are problems in which rate equations do not even appear.

In EQ6 reaction path models, the two types of equations are coupled in the mathematically formal sense, but the solution of each is performed semi-independently. That is, each type of calculation is performed alternately, the output of one becoming the input to the next execution of the other. For example, in moving a step forward in reaction progress, the rate equations are integrated. This defines a new set of total component masses, temperature, and pressure, which are the inputs to the following thermodynamic calculation. This in turn yields a new distribution of species, which then gives values for the rates of the irreversible processes at the new point. These rate values are then used in making the next integration step.

When the rate chosen to constrain an irreversible process is a relative rate, the rate function is either a constant or a simple function of the overall reaction progress variable (ξ). When EQ6 operates in the mode of arbitrary kinetics (all irreversible processes constrained by relative rate expressions, no time variable in the model), these rates can be integrated by

simple closed-form expressions, rather than having to be evaluated numerically. It is therefore possible to take arbitrarily large step sizes, subject only to the following conditions.

In the case of closed and open system calculations, the rate of an irreversible reaction is set to zero when the corresponding thermodynamic driving force, the affinity (see section 3.2.6), is no longer positive. Affinities, as noted above, are outputs from the thermodynamic calculations. EQ6 locates the point of reaction progress where the affinity goes to zero. If the corresponding reactant is a mineral, then this means that the aqueous solution has reached saturation. The code then changes the status of the reactant to inactive (meaning it is effectively removed from the set of reactants). Any remaining mass of the reactant is then moved into the "equilibrium" part of the system. Thus, in arbitrary kinetics, the rate equations remain integrable in closed form, in the "piecewise" sense.

A similar zeroing of irreversible reaction rate occurs when a reactant becomes exhausted, no matter what mode the code is operating in. The user specifies how much of a reactant is available at the start of the run. The code then finds the points of reaction progress at which exhaustion occurs. In the arbitrary kinetics mode, closed form integration of the rate equations proceeds in the "piecewise" sense just as in the case noted above.

The purpose of this chapter is to review the governing equations, the "input constraints" (the "knowns" appearing in these equations), and the "outputs" (the "unknowns" and any parameters calculated from them). In the section that immediately follows, the algebraic equations that govern thermodynamic calculations are reviewed. All of these equations have been discussed in either the EQ3NR user's guide (Wolery, 1983) or the EQ3/6 brine modifications report (Wolery, 1984), although some the equations have some slight differences in the way they pertain to EQ6. The discussion in this report will be as brief as possible. The section after that focuses on the equations dealing with reaction progress, reaction rates, temperature, and pressure.

3.2. CONSTRAINTS ON THERMODYNAMIC CALCULATIONS

3.2.1. Mass Balance

Mass balance in EQ6 takes on a slightly different form than in EQ3NR. All species appearing in the "equilibrium" part of the system contribute to mass balance. In EQ3NR, this system consisted only of the aqueous phase. Here, however, it also includes minerals and other substances in equilibrium with the aqueous solution. A second difference is that in EQ3NR, mass balance was treated in terms of concentrations. In EQ6, it is treated in terms of masses. Molal concentrations (m_s) are related to the corresponding masses (n_s) by the equation

$$m_s = \omega n_s / n_w \quad (3-1)$$

where ω is the number of moles of water in one kilogram (≈ 55.51) and n_w is the number of moles of water present.

The general expression for mass balance for the s' -th master component in EQ6 is given by

$$\sum_s^{s_T} u_{ss'} n_s + \sum_{\varphi}^{\varphi_E} u_{\varphi s'} n_{\varphi} + \sum_{\psi}^{\psi_E} \sum_{\sigma}^{\sigma_{T,\psi}} u_{\sigma\psi s'} n_{\sigma\psi} = n_{s'}^T \quad (3-2)$$

Here s_T is the number of aqueous species in the system, φ_E is the number of minerals of fixed composition present and in equilibrium with the water, ψ_E is the number of such solid solution phases, and $\sigma_{T,\psi}$ is the number of components in the ψ -th solid solution. Also, n_{φ} is the mass of the φ -th pure mineral present, $n_{\sigma\psi}$ is the mass of the σ -th component of the ψ -th solid solution, and $n_{s'}^T$ is the total mass of the s' -th master component. The stoichiometric factors ($u_{ss'}$, $u_{\varphi s'}$, and $u_{\sigma\psi s'}$) relate the contributions of the aqueous, pure mineral, and solid solution components to the mass balance. There is such an equation for each of the

s_0 aqueous master species present in the model except the s_8 -th, the fictive aqueous species $O_2(g)$.

3.2.2. Charge Balance

The charge balance equation comes into the calculations if a redox parameter is needed to complete the model, which is generally the case. The fictive aqueous species $O_2(g)$ is the corresponding master species, and the primary redox parameter is the oxygen fugacity. From this, other redox parameters can be calculated, such as Eh, pe, or Ah (See Wolery, 1983). The charge balance equation can be written

$$\sum_s^{s_T} z_s n_s = 0 \quad (3-3a)$$

where z_s is the electrical charge. This is analogous to equation 3-2 (mass balance), except that the weighting factors are different and there are no terms for non-aqueous components.

In practice, the initializing models computed by EQ3NR may be either charge balanced or out of charge balance. EQ6 can handle either case (earlier versions required charge-balanced input). EQ3NR calculates the charge imbalance at the end of its speciation calculation and writes this parameter [$\Delta(zn)$; the variable ELECTR] on the EQ3NR PICKUP file. EQ6 then adds this term into the electrical balance, so that the initial charge imbalance is maintained throughout the run. In other words, equation 4-3 is modified to

$$-\Delta(zn) + \sum_s^{s_T} z_s n_s = 0 \quad (3-3b)$$

3.2.3. Mass Action

A mass action equation describes thermodynamic equilibrium for a corresponding chemical reaction. The reactions on the EQ3/6 data file are always written as dissociation, destruction, or dissolution reactions. All species but one in each reaction are aqueous master species. The remaining species, which is formally paired with the reaction, is destroyed as the reaction proceeds (See Wolery, 1983). A general expression of the i-th mass action equation associated with the j-th species as treated in EQ3/6 is given by

$$b_{ji} \log x_j + b_{1i} \log a_w + b_{s_B i} \log f_{O_2} + \sum_{s'=2}^{s_Q} b_{s' i} (\log m_{s'} + \log \gamma_j) = \log K_i \quad (3-4)$$

Should this be $s' = s_B$?

Here the reaction coefficients b are negative for reactants and positive for products, following the usual EQ3/6 convention. K is the equilibrium constant. Water is always the first aqueous master species, hence b_{1i} is the reaction coefficient for water. The fictive aqueous species $O_2(g)$ is always the s_B -th species. The symbol s' implies master aqueous species other than $H_2O(l)$ or $O_2(g)$.

In the above equation, b_{ji} is the reaction coefficient for the associated species (the j-th), and x_j is a_j , the thermodynamic activity of the species, unless it is a gas, in which case x_j is f_j , the fugacity. There are currently three possible evaluations of a_j in EQ3/6. If the reaction is an ion-pair or complex dissociation or an aqueous redox destruction reaction, then

$$\log a_j = \log m_j + \log \gamma_j \quad (3-5a)$$

In this case, s'' is generally used to represent the j-th species and r to

denote the corresponding i-th reaction. If the reaction is the dissolution of a pure mineral (a mineral of fixed composition, then

$$\log a_j = 0 \quad (3-5b)$$

and ϕ is generally used to denote both the mineral and the reaction. In the case of the dissolution of the σ -th component of the ψ -th solid,

$$\log a_j = \log x_j + \log \lambda_j \quad (3-5c)$$

Here x is the mole fraction of the component in the solid solution and λ is its activity coefficient. Both the reaction and the component are generally denoted by the double subscript $\sigma\psi$.

3.2.4. Activity Coefficients of Aqueous Species

As implied by the discussion in the above section, thermodynamic calculations require activity coefficients. These functions relate concentrations to thermodynamic activities. Concentration scales must be specified in order to define activities and activity coefficients, as well as concentrations themselves (See Wolery, 1984). The concentration scale used by EQ3/6 for aqueous solutes is the molal scale. Thus, the activity (a) of the s -th aqueous species (excluding the case $s = 1$, which pertains to the solvent, water) is related to its concentration (m) by its activity coefficient (γ) by

$$a_s = m_s \gamma_s \quad (3-6a)$$

or in logarithmic form by

$$\log a_s = \log m_s + \log \gamma_s \quad (3-6b)$$

The activity of water is generally defined by reference to the mole fraction scale (See Wolery, 1984). It is possible to define a corresponding

activity coefficient. However, in practical usage, this is rarely done. Instead, common practice is to deal directly with the activity of water (a_w), as in equation 3-4. Consequently, when one speaks of "activity coefficients," the activity of water is usually implied as well.

Activity coefficients are functions of solution composition, temperature, and pressure. However, there is no universal set of equations for calculating them. Instead, there are various equations that each have their own strengths and weaknesses. Several different approaches have been programmed into EQ3/6 (Wolery, 1984), and the user must choose among them. These options are summarized here because they are central to the usage of EQ3/6.

The activity coefficient option is specified using the option switch IOPG1. The existing options are:

<u>IOPG1</u>	<u>Option</u>
-3	Short form of hydration theory equations
-2	Short form of the Helgeson et al. (1981) equations
-1	The Davies (1962) equation (with a thermodynamically consistent equation for the activity of water)
0	The B-dot equation (Helgeson, 1969) for ionic species, unit activity coefficient for polar neutral species, the activity coefficient of aqueous CO_2 for nonpolar neutral species, and an expression due to Helgeson et al. (1970) for the activity of water
1	Pitzer's (1973) equations
2	Long form of hydration theory equations

The equations for all options except IOPG1 = 0 are thermodynamically consistent. The thermodynamic inconsistency of this one option is not a serious problem, because the accuracy of these equations limits their use to relatively dilute solutions (see below).

The options fall into two categories. In the first (IOPG1 less than or equal to zero), the activity coefficients are, with two simple exceptions, functions of the ionic strength

$$I = 1/2 \sum_{s=2}^{s_T} m_s z_s^2 \quad (3-7)$$

but not of the specific aqueous solution composition. The EQ3NR and EQ6 codes face a simpler problem in running thermodynamic calculations with these options.

One exception occurs in the case IOPG1 = 0, where the activity of water is estimated instead from the equivalent stoichiometric ionic strength of a sodium chloride solution (Helgeson et al., 1970)

$$I_E = \sum_{s=2}^{s_T} u_{ss_E} m_s \quad (3-8)$$

Here s_E denotes either Na^+ or Cl^- (s_E is chosen in running EQ3NR- see Wolery, 1983) and the factor u_{ss_E} represents the stoichiometric equivalence of species s to species s_E . If s_E is not defined, which is sometimes the case, then I_E is defined as zero. This fixes the activity of water at unity ($\log a_w = 0$).

The other exception occurs in the case of IOPG1 = -2, where the activity of water and the activity coefficients both depend on the quantity Σhm

$$\Sigma hm = \sum_{s=2}^{s_T} h_s m_s \quad (3-9)$$

This quantity is the amount of water (per kilogram of nominal solvent) that is bound up as water of hydration of the aqueous solute species. This parameter also is used in the option IOPG1 = 2.

The second category of options pertains to IOPG1 greater than zero. In these options, the activity of water and the activity coefficients depend on the specific composition of the aqueous solution, not just on the ionic

strength. There are two such options currently in EQ3/6, Pitzer's equations and the long form of the hydration theory equations. The long form of the equations of Helgeson et al. (1981) would also fall into this category, but only the simpler short form (Helgeson et al., 1981, equation 298, p. 1478) has been put in up to the present time.

The relevant forms of the equations noted above are given by Wolery (1984) and will not be repeated here. Wolery (1984) also discusses the strengths and weaknesses of these activity coefficient models. For example, the B-dot and Davies equations options are unsuitable for applications in which the ionic strength exceeds one molal. The reader should also be aware of the special data base requirements of some of the options (e.g., hydration numbers for species on the thermodynamic data file DATA0 for hydration theory options, and a special Pitzer coefficient data base and associated data base preprocessor for using Pitzer's equations- See Wolery, 1984).

Additional models can be added by writing new coding to permit evaluation of the following quantities:

1. $\log a_w$
2. $\log \gamma_s$, for $s = 2, s_T$
3. $\Gamma_{wI} = \partial \log a_w / \partial \log I$
4. $\Gamma_{wj} = \partial \log a_w / \partial \log m_j$, for $j = 2, s_T$
5. $\Gamma_{sI} = \partial \log \gamma_s / \partial \log I$, for $s = 2, s_T$
4. $\Gamma_{sj} = \partial \log \gamma_s / \partial \log m_j$, for $s = 2, s_T$, and $j = 2, s_T$

The activity of water and the activity coefficients are evaluated in subroutine GCOEFF. The partial derivative quantities are computed by subroutine GMCALC. Both of these routines reside in the EQLIB library. Addition of a new set of equations also requires, of course, the input of any necessary supporting data not currently part of EQ3/6, and defining a value of IOPG1 to correspond to the new option.

3.2.5. Activity Coefficients of Solid Solution Components

The activities and activity coefficients of solid solution components are usually defined on the mole fraction scale. The relationship is as shown in equation 3-5c, where the activity coefficient is symbolized by λ (compare 3-5c with 3-6b).

The status of the treatment of solid solutions in EQ3/6 is currently limited to simple molecular mixing models. These are models in which the components are end members, which are equivalent to pure minerals. The existing capabilities are described elsewhere (Wolery, 1979, Table 3, pp. 12-13) and require coding not only for evaluating λ , but also the derivative function $\Lambda_{ij} = \partial \log \lambda_i / \partial \log x_j$, where x stands for mole fraction. These capabilities will not be repeated here in view of the currently primitive level of development of solid solution modeling in EQ3/6.

3.2.6. Saturation Indices and Affinities

Saturation indices and affinities are important because they are measures of the thermodynamic driving forces behind the progress of irreversible reactions. These quantities form an important bridge between calculations that are purely thermodynamic and those that pertain to dynamic evolution. If there is no positive driving force for a reaction, it will not proceed in the forward direction. No matter what rate constraints the user may specify for irreversible reactions, EQ6 always truncates such a rate (sets it to zero) when the corresponding driving force is zero or opposed to further progress. The affinity function also appears directly as a parameter in some important kinetic rate laws (See Section 3.3.3).

The saturation index (SI) is a commonly used measure of the state of an aqueous solution with respect to the progress of some reaction, usually the dissolution of a mineral. It is defined

$$SI = \log Q_d - \log K_d \quad (3-10)$$

where Q is the ion activity product (IAP), K is the equilibrium constant, and the subscript "d" denotes that Q and K pertain to the reaction as written for the dissolution/dissociation/destruction of the associated species. The reactions on the EQ3/6 data file are always written this way. Saturation indices are zero for the case of exact saturation, negative for undersaturation, and positive for supersaturation.

In EQ3/6 nomenclature, Q is evaluated for the i-th reaction according to

$$\begin{aligned} \log Q_{d,i} = & b_{ii} \log a_i + b_{li} \log a_w + b_{s_{B}i} \log f_{O_2} \\ & + \sum^{s_Q} b_{s,i} (\log m_{s,i} + \log \gamma_{s,i}) \end{aligned} \quad (3-11)$$

$\begin{matrix} s'=2 \\ s'=s_B \end{matrix} \longrightarrow s' = s_2$

Here the term in $\log a_i$ is evaluated using equation 3-5a for aqueous reactions, by 3-5b for pure minerals, and 3-5c for solid solution components. The redox affinity (Ah; Wolery, 1983) results when 3-10 and 3-11 are applied to half-reactions. In the case of gas components, $\log f_i$ must be substituted for $\log a_i$.

The saturation index of the ψ -th solid solution phase can be constructed from the saturation indices of its components (σ) and their mole fractions (x) according to

$$SI_{\psi} = \sum_{\sigma=1}^{\sigma_{T,\psi}} x_{\sigma} SI_{\sigma\psi} \quad (3-12)$$

The affinity is closely related to the saturation index. Affinities may be defined for both the forward ("+") and reverse ("-") directions of a

reaction. In EQ3/6, "forward" means in the direction of dissolution/dissociation/destruction of the associated species, so "+" corresponds to "d". Hence, "-" signifies precipitation/association/production of the associated species.

Following these conventions, the affinity to dissolve/dissociate/be destroyed is related to the saturation index by

$$A_+ = - 2.303 RT SI \quad (3-13)$$

and the affinity to precipitate/associate/be formed is

$$A_- = + 2.303 RT SI = - A \quad (3-14)$$

When the affinity is positive, it means that the reaction is thermodynamically favored to move in the corresponding direction. Note that affinity has the dimensions of energy per mole (of reaction progress). Also, the affinity to precipitate/associate/be formed follows that same sign conventions with respect to supersaturation/undersaturation as the saturation index.

3.3. CONSTRAINTS RELATED TO REACTION PROGRESS

3.3.1. The Reaction Progress Variable

The reaction progress variable (ξ) is a measure of the extent to which a reaction has proceeded. Any chemical reaction can be written in the following format



Here A, B, etc. are reactants, C, D, etc., are products, and a, b, c, d, etc., are the reaction coefficients (all positive when written in this form). There are two equivalent ways to describe a chemical process. The first is to consider it as an array of reactions. Here the reaction coefficients are constants and are usually chosen to be small integers or common rational numbers such as 1/2, 1/4, etc. The second is to view the whole process as a single reaction, whose reaction coefficients are generally neither such "nice" numbers nor even constants along a reaction path.

In EQ6, reaction progress variables are used to describe only the reactions that are irreversible (not at equilibrium). The irreversible process is defined by an array of irreversible reactions of the type described above. Each of these has its own associated progress variable (ξ_i). There is in addition an overall reaction progress variable (ξ) for the process as a whole, which corresponds to the second case described above.

It is possible to define progress variables for reversible reactions as well. This is done in some methods for making thermodynamic calculations (See Van Zeggeren and Storey, 1970), in which case these parameters are used as iteration variables in place of masses or concentrations of component species. (In this usage, reaction progress variables are generally symbolized by λ instead of ξ .) This type of treatment is not used in EQ6, however.

Reaction progress variables are commonly defined in the following differential form (e.g., Helgeson, 1968; Lasaga, 1981a)

$$d\xi_i = - (1/a_i) dn_{A,i} = + (1/c_i) dn_{C,i} = \dots \quad (3-16a)$$

$$d\xi = - (1/a) dn_A = + (1/c) dn_C + \dots \quad (3-16b)$$

The total change in the mass of a component must be the sum of the changes due to the individual reactions. Hence,

$$dn_A = \sum_{i=1}^{i_T} dn_{A,i}, \text{ etc.} \quad (3-17)$$

where i_T is the total number of individual irreversible reactions. Then coefficients of the overall reaction are related to those of the individual reactions by

$$a = \sum_{i=1}^{i_T} a_i (d\xi_i/d\xi), \text{ etc.} \quad (3-18)$$

The quantity $d\xi_i/d\xi$ is called the relative rate of the i -th irreversible reaction.

The motivation behind the reaction progress variable is to normalize the effect of the reaction coefficients that appear in a given reaction. Recasting equations 3-16 in terms of derivatives, we get the series of equations

$$- dn_A/d\xi_i = a_i, + dC/d\xi_i = c_i, \text{ etc.} \quad (3-19a)$$

$$- dn_A/d\xi = a, + dC/d\xi = c, \text{ etc.} \quad (3-19b)$$

These equations lead to the derivative equivalent of equation 3-17

$$dn_A/d\xi = \sum_{i=1}^{i_T} dn_A/d\xi_i, \text{ etc.} \quad (3-20)$$

Following the usual EQ3/6 convention for writing reactions on the data file, the reaction coefficients (b) are intrinsically negative for reactants. Switching to this notation, equations 3-19 can be rewritten for the j-th component without regard to whether it is a reactant or a product

$$dn_j/du_i = b_{ji} \quad (3-21a)$$

$$dn_j/du = b_j \quad (3-21b)$$

where b is the coefficient of this component in the overall reaction.

Restating equation 3-18,

$$b_j = \sum_{i=1}^{i_T} b_{ji} (d\xi_i/d\xi) \quad (3-22)$$

It should be clear that changes in the quantities of the components A, B, C, D, etc., can be obtained by integrating with respect to the appropriate progress variable. For the case of an individual reaction, this gives

$$\Delta n_{j,i} = \int_{\xi_{i,1}}^{\xi_{i,0}} b_{ji} d\xi_i \quad (3-23)$$

where the subscripts 1 and 0 signify two successive points along the reaction path (with ξ_0 greater than ξ_1). Because the coefficients b_{ji} are constants, equation 3-23 yields

$$\Delta n_{j,i} = b_{ji} \Delta \xi_i \quad (3-24)$$

where $\Delta \xi_i = \xi_{i,0} - \xi_{i,1}$.

Equation 3-24 leads to a more immediate understanding of the reaction progress variable. Basically, it says that the change in the mass of component j due to reaction i is proportional to ξ_i . Thus, when $\xi_i = 1$, $\Delta n_{j,i} = b_{ji}$.

The overall reaction equivalent of equation 3-23 is

$$\Delta n_j = \int_{\xi_1}^{\xi_0} b_j d\xi \quad (3-25)$$

However, the overall reaction coefficient b_j is not in general a constant. Substituting equation 3-22 into 3-25 and integrating gives

$$\Delta n_j = \sum_{i=1}^{i_T} [b_{ji} \Delta \xi_i] \quad (3-26)$$

This is the central equation used to calculate irreversible mass transfer in EQ6. Note that it depends on integrating the relative rates ($d\xi_i/d\xi$) with respect to the overall reaction progress variable.

3.3.2. Reaction Rates and Time

The user of EQ6 specifies for each irreversible reaction a function for either the relative rate or the actual rate ($d\xi_i/dt$). If a relative rate function is specified, then the evaluation of equation 3-26 is straightforward. If an actual rate is specified, then a relative rate function is derived from this as shown below. Time is not defined unless at least one actual rate specification is included in the model to be calculated. The scheme used here to handle relative rates and time when calculating a kinetic reaction path is essentially the same as that described by Helgeson and Murphy (1983). It is slightly different in that the approach is extended to allow mixing of relative rates with actual rates in specifying a problem.

In arbitrary kinetics, ξ is simply the integration variable and no further definition is required. In actual kinetic calculations, this is not the case. A convenient definition is

$$\xi = \sum_{i=1}^{i_K} \xi_i \quad (3-27)$$

where i_K is the number of irreversible reactions constrained by actual rate laws. The motivation behind this definition becomes apparent by differentiating it with respect to time, which gives

$$d\xi/dt = \sum_{i=1}^{i_K} d\xi_i/dt \quad (3-28)$$

Having defined $d\xi/dt$, we can now calculate relative rates for the irreversible reactions constrained by actual rates

$$d\xi_i/d\xi = \frac{d\xi_i/dt}{d\xi/dt} \quad (3-29)$$

Similarly, we can also now calculate actual rates for irreversible rates which are constrained by relative rates

$$d\xi_i/dt = (d\xi_i/d\xi) (d\xi/dt) \quad (3-30)$$

It is also then possible to calculate the inverse rate, defined as

$$dt/d\xi = \frac{1}{d\xi/dt} \quad (3-31)$$

A time increment can be calculated for a reaction progress step by integrating the inverse rate (Helgeson and Aagaard, 1979; Helgeson and Murphy, 1983)

$$\Delta t = \int_{\xi_1}^{\xi_0} (dt/d\xi) d\xi \quad (3-32)$$

3.3.3. Rate Laws Programmed into EQ6

There are no specific restrictions on the forms of rate laws that can be programmed into EQ6. However, any rate law to be used must be coded into subroutine RTCALC. It is not necessary to program any expressions for the derivatives of the rate laws. The rate laws must be written in terms of parameters that currently appear in the code. For example, Lasaga (1981a) proposed a rate law for feldspar dissolution that is explicitly linked to the sorption of hydrogen ion on the feldspar surface. Such a rate law can not be dealt with in the current version of EQ6, because there is no provision for sorption (surface chemistry) phenomenon (though development of such is planned). Also, at the present time, the use of kinetic rate laws is restricted to the dissolution of solids (again, more development is planned).

The rate law to be used for the NRC-th irreversible reaction is specified on the INPUT file (See Chapter 5) by the parameter NRK(NRC). The currently programmed rate laws include

<u>NRK</u>	<u>Rate Law</u>
0	Relative rate
1	Transition-state theory
2	Affinity-to-a-power rate law
3	Linear plus parabolic rate law

Some rate laws yield rates that go to zero when the affinity goes to zero, and others do not. It is important to remember that EQ6 truncates the rate (sets it to zero) in the absence of a favoring thermodynamic driving force.

There is no justification for the use of elaborate expressions as rate laws for relative rates. If there is more than one irreversible reaction in a set, then rigorous treatment of relative rates requires specifying kinetic rate laws and allowing relative rates to be calculated according to equation

3-29. The use of relative rate specifications is less exact, but often very useful nonetheless.

Only one expression for relative rates is currently programmed into EQ6, a truncated second-order Taylor's series in overall reaction progress:

$$d\xi_i/d\xi = \rho_{1i} + \rho_{2i}\xi + (1/2!) \rho_{3i}\xi^2 \quad (3-33)$$

Here ρ_{ji} is the j -th derivative of ξ_i with respect to ξ at $\xi = 0$. Values for ρ_{ji} are entered on the INPUT file when this rate law is selected. Normally, relative rates are specified as constants; i.e., $\rho_{1i} = \rho_{3i} = 0$. Picking reasonable values for relative rates is not easy even then. One useful rule of thumb when modeling the interaction of a rock with a water is to pick the relative rates of dissolution of the minerals in the rock such that they are proportional to their abundances. 0 2 i

The transition-state theory rate law is programmed in the form

$$d\xi_i/dt = f_i s_i \sum_{m=1}^{m_{T,i}} k_{mi} \left(\prod_j^{j_{T,mi}} a_j^{-n_{jmi}} \right) (1 - e^{-A_i/\sigma_{mi}RT}) \quad (3-34)$$

Here s_i is the total surface area of the phase dissolving in the i -th irreversible reaction and f_i is a fudge factor representing the proportion of effective to total surface area. Normally, f is taken as unity. The summation is over $m_{T,i}$ parallel mechanisms for the i -th irreversible reaction (here m is used as an index for mechanisms, not to represent molal concentrations).

Here also k_{mi} is the rate constant, $j_{T,mi}$ is the number of activity factors for the m -th mechanism of the i -th reaction, which may be zero, a_j is the thermodynamic activity of an aqueous species whose identity is implied by i , m , and j , and n_{ji} is the corresponding exponent. The symbol Π is the multiplicative equivalent of \sum . Here also A_i is the affinity to dissolve (A_d or A_+ in previous parlance), R is the gas constant, and T is the absolute temperature. The parameter σ_{mi} is a stoichiometric adjustment factor. It is the ratio of the number of moles of solid destroyed n_{jmi}

in the macroscopic reaction to the number of moles of the corresponding activated complex destroyed in the microscopic reaction. It is nearly always unity.

Note that this rate law is a function of the chemistry of the aqueous solution, but is not an explicit function of time. This rate law yields a rate that goes to zero as the affinity goes to zero. For further discussion and examples of the usage of this rate law, see Aagaard and Helgeson, 1977, 1982; Helgeson and Aagaard, 1979; Helgeson and Murphy, 1983). The rate law of Rimstidt and Barnes (1980), though written in a slightly different form, is equivalent to the above equation.

The affinity-to-a-power rate law is simply

$$d\xi_i/dt = f_i s_i k_i A_i^{n_i} \quad (3-35)$$

Here the parameters are as given in the discussion of the previous rate law, except n_i , which is the exponent of the affinity. This form is also a function of chemistry but not explicitly of time. It too yields a rate law that goes to zero as the affinity goes to zero.

The linear-plus-parabolic rate law is a simple form explicit in time

$$d\xi_i/dt = k_{1i} + k_{2i} (t - t_0)^{1/2} \quad (3-36)$$

Here k_{1i} is the linear coefficient, equal to the linear part of the rate, and k_{2i} is the parabolic coefficient. The parameter t_0 is the time the parabolic mechanism (assumed to be diffusion-controlled) began to operate. Normally, $t_0 = 0$. There is no dependence on chemistry, which is unrealistic. However, this rate law is of some usefulness. With $k_{2i} = 0$, it permits the user to define a constant rate.

3.3.4. Temperature and Pressure

In most EQ6 runs, the temperature and pressure are constants. However, for many processes, the temperature and/or pressure change along the reaction path. EQ6 is set up to deal such changes, provided that the user defines these changes as functions of the overall reaction progress variable or of time.

At the present time, EQ6 does not make corrections for pressures off the pressure-temperature curve established on the data base. The standard curve is 1.013 bar (1 atm) up to 100°C, and the steam/water curve at higher temperatures. Thus, pressure is currently parameterized as a function of temperature. Plans call for removing this limitation in further development. At that time, pressure should be treatable in the same fashion as for temperature.

Temperature is directly specified as a function of overall reaction progress or time. The choice of the function is otherwise dictated by the problem at hand. However, the only functional form currently programmed into the code treats temperature as a third-order truncated Taylor's series:

$$T = T_0 + (dT/dx) x + (1/2!) (d^2T/dx^2) x^2 + (1/3!) (d^3T/dx^3) x^3 \quad (3-37)$$

Here T_0 is the temperature at $x = 0$ and x stands for either ξ or t .

4. TYPES OF EQ6 CALCULATIONAL MODELS

4.1. INTRODUCTION

EQ6 calculational models can first be broken down into "single-point" thermodynamic equilibrium calculations and reaction path calculations. A "single point" thermodynamic calculation is essentially just the special case of a reaction path with no steps. Reaction path calculations may be broken down into computations for titrations, irreversible reaction in closed systems, and irreversible reaction in certain well defined types of open systems. Such calculations may be kinetic or non-kinetic (arbitrary kinetics), depending on whether or not the time variable is part of the model.

The purpose of this chapter is to discuss the various kinds of calculations EQ6 is capable of making, to note the assumptions peculiar to the different kinds of calculational scenarios, and to introduce some of the corresponding key INPUT file parameters. A comprehensive description of the INPUT file and the parameters appearing on it is given in Chapter 5.

4.2. "SINGLE-POINT" THERMODYNAMIC CALCULATIONS

4.2.1. General Discussion

"Single point" thermodynamic calculations are useful for several purposes. For example, suppose an EQ3NR calculation shows that an aqueous solution is supersaturated with several minerals. An EQ6 "single point" calculation can find which of possibly many such minerals would actually be present if the system were to reach thermodynamic equilibrium. A particular type of "single point" computation, the so-called "temperature jump," can be

used to calculate the high temperature, in situ pH and other properties of an aqueous fluid in an autoclave experiment from measurements on quenched fluid samples. A "single point" calculation is specified on the EQ6 INPUT file by setting KSTPMX = 0. KSTPMX is the maximum number of steps of reaction progress that will be taken before the program terminates execution of the current problem.

4.2.2. Precipitating Supersaturated Phases

An aqueous solution may be supersaturated with respect to a large number of minerals. EQ6 can be used to calculate the assemblage of aqueous solution plus minerals that would result if the aqueous system reached thermodynamic equilibrium. In general, only a few of the phases that supersaturate the solution prior to precipitation appear in the final assemblage. This is a result of the common ion effect; e.g., if the water is supersaturated with respect to more than one aluminum-bearing mineral, precipitation of any one of these minerals reduces the concentration and thermodynamic activity of Al^{3+} , thereby lowering the saturation index for each aluminum-bearing minerals. EQ6 finds the correct phase assemblage through a trial-and-error process governed by algorithms discussed in Chapter 7. As part of the calculation, EQ6 determines any changes in the solvent mass, pH, Eh, etc., that result from the precipitation of the mineral phases. An example of such a calculation is given in Section 6.2.1.

This type of calculation occurs at the beginning of every EQ6 calculation, whether or not it is "single point." Precipitation of supersaturated phases (so that no solubility equilibrium is violated) is a default condition. Any mineral loaded into memory is eligible to be precipitated unless the user acts to suppress it. This may be done using either the sub-set selection suppression options (See NXOPT, UXOPT, described in Chapter 5) or the individual species suppression options (See NXMOD, UXMOD). Exceptions to the sub-set selection options may be specified (See NXOPEX, UXOPEX). By using the "ALL" sub-set selection suppression option in conjunction with the exceptions

option, the user may specify just those minerals which are not to be suppressed.

4.2.3. The Temperature Jump

A "temperature jump" occurs when the temperature at the start of an EQ6 calculation does not match that corresponding to the initializing calculation done by EQ3NR or a previous run of EQ6. Temperature jumps may occur at the start of a reaction path calculation, as well as in a "single point" calculation. At the present time, pressure is parameterized as a function of temperature (a limitation of the current thermodynamic data file), so a corresponding "pressure jump" may occur as well. When generalized pressure corrections are available in EQ6, independent pressure jumps will be possible.

EQ6 detects a temperature jump by calculating the starting temperature from the governing parameters specified in the first part of the INPUT file (TEMPCO, JTEMP, TK1, TK2, and TK3; see Chapter 5) and comparing it with the temperature of the previous calculation (TEMPCI, written on the second part of the INPUT file).

The temperature jump is useful for calculating the thermodynamic properties of an aqueous solution when the measurements (as of pH, Eh, etc.) pertain to samples of the fluid that have been heated or cooled from the temperature of interest (such as the in situ temperature of an autoclave). Such sampling and measurement are normally carried out so as to avoid mineral precipitation. Thus, all mineral precipitation should be suppressed in the calculations. The sub-set selection suppression "ALL" is convenient for this purpose. Thus, one can use EQ6 to estimate the in situ or "at temperature" pH in an autoclave experiment from measurements including the quench (room temperature) pH. Other properties, such as the in situ oxygen fugacity, Eh, pe, saturation indices, reaction affinities, and equilibrium gas fugacities, also result from such a calculation. An example of such a calculation is given in Section 6.2.2.

It is also possible to use a "single point" temperature jump calculation to find the quench properties that correspond to a fluid generated in an elevated temperature reaction path calculation. For purposes of comparing experimental results with theoretical simulations, it is better to estimate the in situ properties from the experimental results than to calculate the quench properties corresponding to the simulations. This is because a fairly large number of simulations may be required in a study of a single experiment, and the number of "single point" calculations of quench properties would far exceed the number of required in order to calculate the in situ properties.

4.3. REACTION PATH CALCULATIONS

There are three major modes of reaction path calculation in EQ6: titration, closed system, and fluid-centered flow-through open system (selected on the INPUT file by NMODL1 = 1, 2, and 3, respectively). Another possible mode, not currently implemented in EQ6, would be a solid-centered flow-through open system (if added, this option will be invoked by NMODL1 = 4). Any of these modes can be modified so that the system behaves as though open to a large external reservoir of gas. This results in models with fixed fugacities for the relevant gas species. The "closed" system mode is partially open under this option.

A few words are in order about the length and complexity of reaction path calculations. The step size control mechanism is a major factor in determining the run time. EQ6 generates finite-difference approximations of the iteration variables used in the thermodynamic calculations, using data from the most recent points of reaction progress. It uses these to generate starting estimates at a new point. The step size is normally constrained to a range in which these approximations are accurate. Furthermore, EQ6 also normally constrains the step size in the process of locating phase boundaries (where a phase either appears or disappears). A consequence of these step size control factors is that the state of the reacting system is usually calculated at numerous points of reaction progress between those for which

printed or plotted output is generated. This has had the effect of making EQ6 look less efficient than some other codes, notably PHREEQE (See INTERA, 1983c).

When operating in the kinetic mode, the finite-difference predictor functions (here generated for both iteration variables and rate functions) must be kept accurate in order to get an accurate integration. The normal phase boundary location constraints must also be operative. Full accuracy constraints are also required for any type of flow-through model, whether kinetic or not. However, in the non-kinetic mode with NMODL1 = 0 or 1, significant savings of execution time may be achieved by relaxing the step size constraints.

Such savings can be achieved in two ways. First, "economy" calculational mode can be selected by setting NMODL2 = 1 (See Chapter 5). This loosens the general step size constraints associated with maintaining accuracy in the finite-difference predictor functions. It causes EQ6 to operate in a calculational mode more like that of PHREEQE (Parkhurst et al., 1980; INTERA, 1983a). "Economy" mode does not compromise the code's abilities to locate phase boundaries. However, additional savings can be achieved by turning off these calculations as well. This can be done by setting IOPT2 = 2, which turns off the phase boundary search function (IOPT2 = 1, the option for printing estimates of phase boundary locations without a rigorous search, is disallowed if NMODL2 = 1).

4.3.1. Simulating a Titration Process

4.3.1.1. General Discussion

A titration process involves the addition of reactants to a system. This option is selected in EQ6 by setting NMODL1 = 1 on the INPUT file. The titration mode of EQ6 is strictly non-kinetic, so only relative rate specifications can be made. The processes given below as examples of

calculations that can be done in the titration mode (fluid mixing, evaporation) can also be handled using the closed (NMODL1 = 2) and flow-through open system (NMODL1 = 3) options, and the use of these other modes would be required in order to include any actual kinetics in the model.

The titration concept is illustrated in Figure 2. At each step of reaction progress, a small quantity of each reactant is added to the contents of the flask, which consist of the aqueous solution and any secondary phases. After each addition, the reactant material dissolves in the water and any secondary phases may grow. At the present development of EQ6, all secondary phases are in equilibrium with the aqueous solution (because precipitation kinetics options have not yet been added to the code). Usually some secondary phases are transients- that is, phases that disappear later on in the process. The growth and dissolution of such phases proceeds at whatever rate is required to maintain solubility equilibrium.

If the aqueous solution becomes saturated with a reactant (in equilibrium with it), then the substance continues to be titrated into aqueous system according to the governing relative rate law. In the titration mode, the calculated rate functions are not truncated by the absence of a thermodynamic driving force, as they are under the closed (NMODL1 = 2) and open (NMODL1 = 3) system options. However, the mass increments under the condition of saturation effectively do not dissolve, but merely accumulate as secondary mass of the same substance.

A reactant that is titrated into the system can be any kind of substance- a mineral, non-mineral crystalline solid, a glass phase, a "whole" rock, a gas, an aqueous species, or even another aqueous solution. The key point is that each reactant must have some stoichiometry. It may or may not have any defined thermodynamic stability (if not, then it is always unstable, and there is no possible saturation condition). A more detailed discussion about reactants and how the user of EQ6 deals with them can be found in Chapter 5.

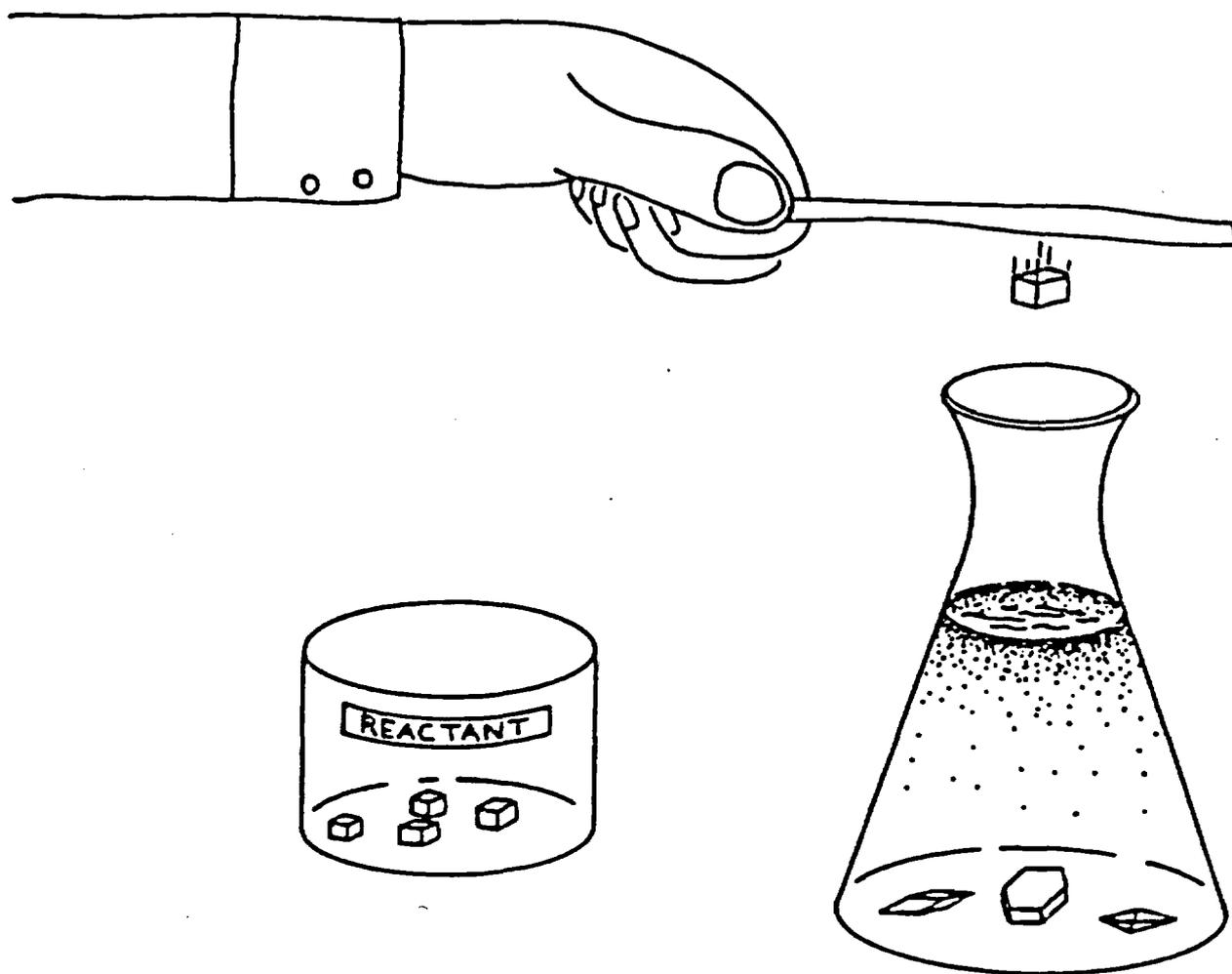


Figure 2. Conceptual model of a titration process (After Wolery, 1980). A reactant (small cubes) is added to an aqueous "equilibrium" system (the flask) in small increments. This system re-equilibrates "instantaneously," which may result in the formation and growth of secondary solids (crystals at the bottom of the flask) by precipitation according to equilibrium solubility. Mass transfer to and from the overlying gas phase is normally ignored (but see section 4.3.5).

4.3.1.2. Fluid Mixing

A good example of a titration model is fluid mixing. The reactant in this case is a second aqueous solution. It is entered on the INPUT file as a "special" reactant (JCODE = 2). The composition of one mole of this substance follows (UESRB and CESRB denote the names and number of moles of component per mole of each component, respectively). For aqueous solution reactants, the recommended procedure is to equate one "mole" with the mass of solution containing 1 kg of solvent water. The composition of such a phase must be determined by a separate EQ3NR calculation.

One aspect of fluid mixing calculations in EQ6 is that the mass of the system being titrated, and the contained mass of solvent water, increases dramatically. At $\xi = 0$, the mass of solution is = 1 kg and the solvent mass = 1 kg (barring any equilibration at this point). At $\xi = 1$, using the above recommended definition of one "mole" for an aqueous solution, the mass of solution is = 2 kg and the mass of solvent water is also = 2 kg.

It is possible to run such a calculation in which the two waters being mixed have different temperatures (See Chapter 5). Here, the user specifies the option JTEMP = 1. The temperature of the first aqueous solution (the one the second is being titrated into) is specified as TEMPCO. The temperature of the second water is given as TK2. The ratio of the mass of the first water to that contained in one "mole" of the second is specified as TK1. With the above definition of one "mole" of aqueous solution, TK1 = 1. The temperature calculation currently assumes that the heat capacity of the two initial waters and all mixtures of the two is the same.

4.3.1.3. Evaporation

Evaporation can be thought of as a sort of negative titration, in which the titrating substance, solvent water, is removed from the system rather than added to it. An evaporation run is easily set up by declaring $H_2O(1)$ a reactant and specifying a negative relative rate. If $d\xi_i/du$ is set to -1, then each unit advancement of ξ corresponds to the removal of 1 mole of solvent. Recall that the number of moles of water in 1 kg is about 55.51. Assuming the usual case in which there is an amount of aqueous solution containing 1 kg of solvent, the upper practical limit on ξ (specified by the parameter ZISTOP, see Chapter 5) would be about 50 or so. If the extent of evaporation would increase the ionic strength above about one molal, the user should specify an activity coefficient option that is valid or highly concentrated salt solutions (See Section 3.2.4).

4.3.2. Calculating the Reaction Path in a Closed System

Calculating the reaction path in a closed system is conceptually and calculationaly very similar to the case of computing a simulation of a titration process. This option is specified on the INPUT file by $NMODL1 = 2$. The conceptual process is illustrated in Figure 3 (Compare with Figure 2). An example of such a calculation is presented in section 6.3.1. The chief difference is that the unreacted masses of reactants are considered to be "in the system," instead of "outside it." A small increment of the remaining mass of each reactant dissolves at each step of reaction progress. The effect is the same as in the titration model, with one exception.

In the closed system, a reactant that saturates may be treated in one of two ways. If a precipitation kinetics rate law is specified for such a reactant, then the unreacted mass is treated according to the rate law specifications, as is the case under the titration option. However, if no

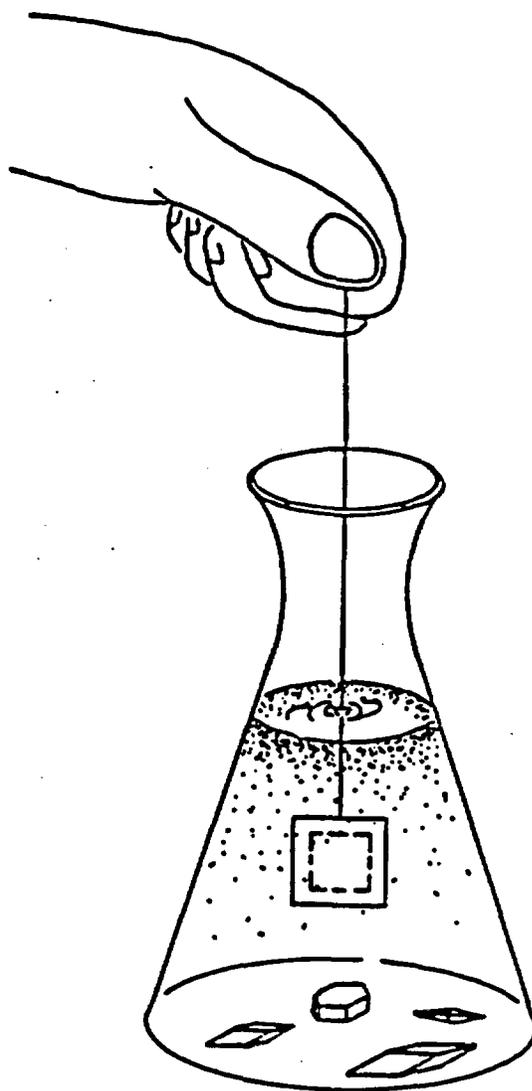


Figure 3. Conceptual model of irreversible reaction in a closed system (After Wolery, 1980). The reactant is represented by the large cube, which dissolves in increments represented by layers.

such rate law is specified, then all of the unreacted mass is immediately transferred to secondary mineral status. The governing rate function is then set to zero. This is primarily a consequence of there being no material left to react, although it is also true that some rate laws (Recall Section 3.3.3) evaluate to zero when the driving affinity is zero. In this case, the rate description of the formation/dissolution of the phase shifts from the specified rate law to the rate that is consistent with keeping the reaction at equilibrium.

4.3.3. A Fluid-Centered Flow-Through System

The fluid-centered flow-through system is a special type of open system which follows the evolution of a particular packet of water as it flows through some medium. This medium could be a fracture, a pipe, or a porous medium. The concept is illustrated in Figure 4. Reactants are presumed to line the medium in homogeneous fashion and interact with the fluid packet as it passes by. Or, there may be no reactants, only a change in temperature or pressure. Either way, secondary phases form as a result. However, as the packet moves on, it leaves behind the masses of secondary phases produced. The result is that transiently formed product phases do not have the opportunity to redissolve in that particular packet of fluid. A consequence is that overall equilibrium can be achieved sooner in terms of reaction progress than is the case in the closed system.

Calculationally, it is not necessary to separate the masses of secondary pure minerals at each step of reaction. It is only necessary to make sure that no mass (actually there is a small but finite limit) of any such phase is destroyed. More of a problem results when solid solution products are involved. Because their composition is in general continually changing, they must be removed as they form. This is not done on every reaction progress step, but is rather governed by a "dump interval" parameter called DLZIDP, which causes such a transfer of material every DLZIDP units of ξ . If only

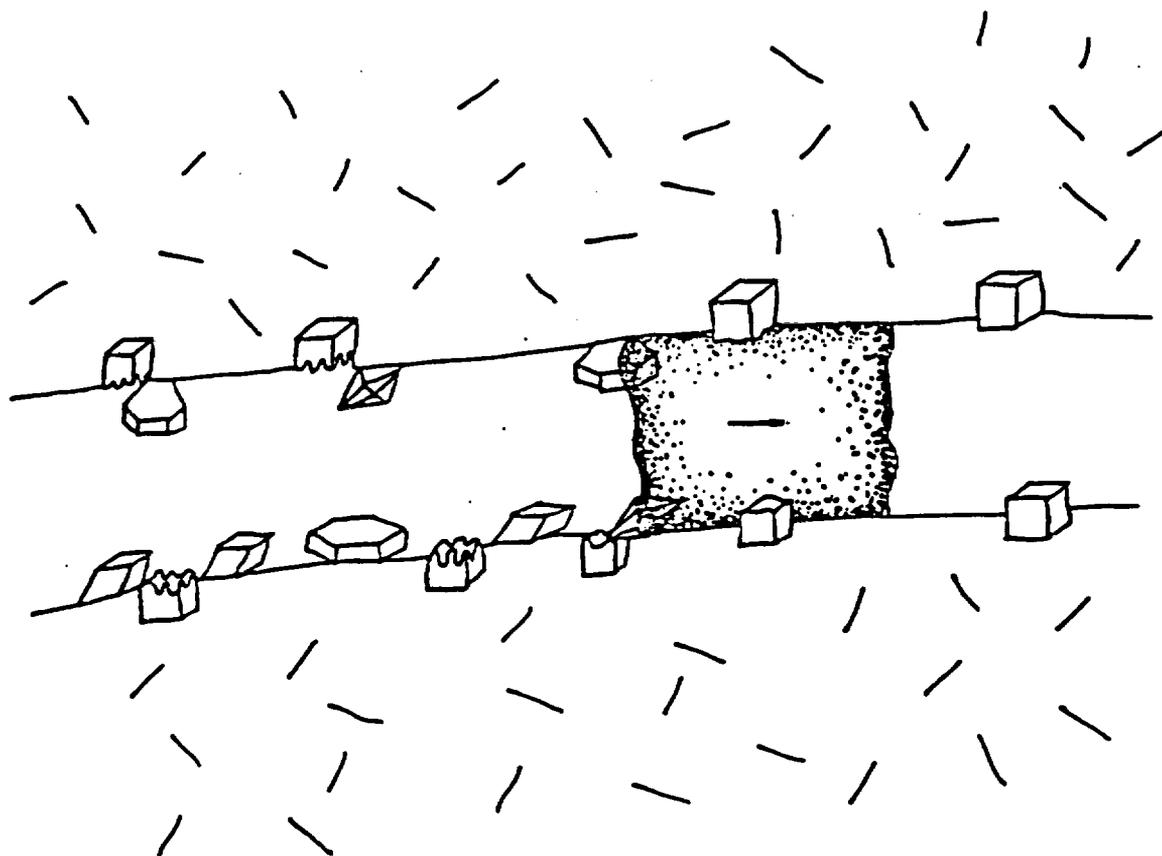


Figure 4. Conceptual model of irreversible reaction in a fluid-centered flow-through system (After Wolery, 1980).

pure minerals are allowed to form, the default value of DLZIDP is pseudo-infinite (and therefore has no effect on the calculation).

4.3.4. A Solid-Centered Flow-Through System

A fundamentally different type of flow-through system would focus on the evolution of solids interacting with a mass of fluid which is either continuously or discretely recharged by a fresh supply of aqueous solution of fixed composition. This concept is illustrated in Figure 5. Such an option is not currently programmed into EQ6. This system closely matches the scenario in many flow-through interactions experiments (for example, the feldspar dissolution rate experiments reported by Knauss and Wolery, 1984). The system of primary and secondary solids and the mass of aqueous phase about them is equivalent to the contents of a leaching cell. The replacement water must be specified as a reactant, and appropriate specification of the replacement process must also be made. The input of fresh aqueous solution is balanced by the output of an equivalent mass.

4.3.5. Systems Open to External Gas Reservoirs

This option has been described elsewhere (Delany and Wolery, 1984). It assumes that the reacting system (of any of the above discussed types) is in contact with a large external gas reservoir, such that specified gas species move to or from that reservoir in order to maintain specified fixed fugacities in the reacting system. Models of this type may be appropriate for describing weathering at the earth's surface, reactions in soils, geochemical interactions in partially saturated (in the hydrologic sense) rock formations, and reactions in certain kinds of experimental configurations. The gas species most likely to be appropriately treated by this option are O_2 and CO_2 .

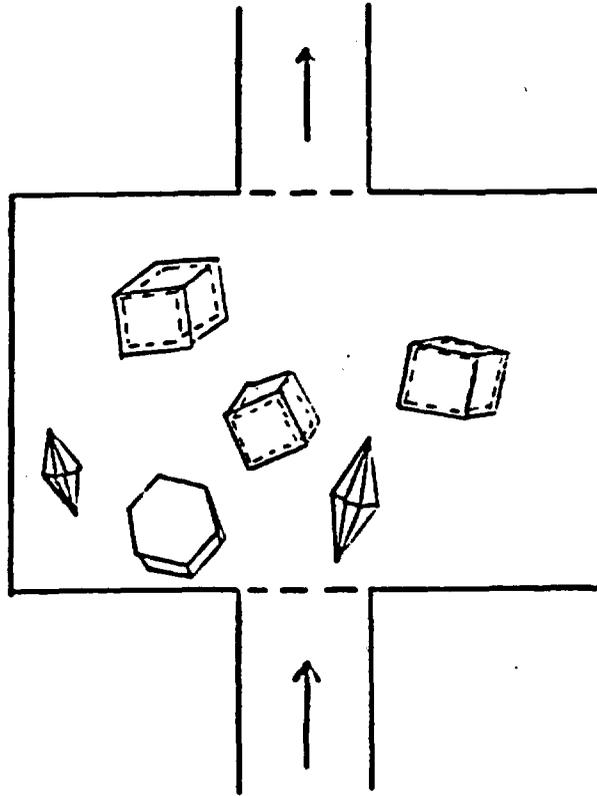
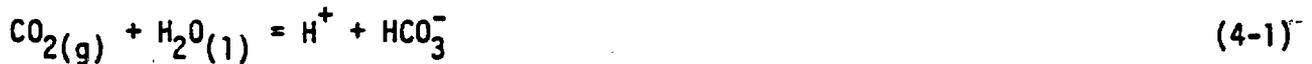


Figure 5. Conceptual model of irreversible reaction in a solid-centered flow-through system. Water flows in at a constant composition, and flows out at another, variable composition.

This option is invoked by specifying each gas to be so treated, the desired fugacity, and an optional mass of the gas to be added to the system at the start of the run. Calculationally, the "external reservoir" is treated as part of the reacting system, and the desired fugacity is maintained by the solubility equilibrium for a fictive mineral whose composition is identical to that of the gas. Without the presence of such a phase, the desired fugacity is really only an upper limit. That is the reason for the option to add mass of the gas component to the system- it permits the user to "saturate" the system. The mass of such a fictive mineral is finite and may be exhausted. The user may wish to choose the initial addition of mass of gas to the system in order to define a point at which the "external reservoir" of the gas is exhausted.

The idea behind using a fictive mineral is as follows. Reactions for the dissolution of gas species are maintained on the data file in order to permit the calculation of equilibrium fugacities. Such a reaction is illustrated by the case for CO_2 :



The corresponding mass action equation is

$$\log a_{\text{H}^+} + \log a_{\text{HCO}_3^-} - \log f_{\text{CO}_2} - \log a_{\text{w}} = \log K_{\text{CO}_2(\text{g})} \quad (4-2)$$

Now consider the parallel reaction for the dissolution of the corresponding fictive mineral ($\text{CO}_2(\text{s})$):



The corresponding mass action equation is

$$\log a_{\text{H}^+} + \log a_{\text{HCO}_3^-} - \log a_{\text{w}} = \log K_{\text{CO}_2(\text{s})} \quad (4-4)$$

(Recall that the thermodynamic activity of a pure solid is unity.)

Subtracting 4-1 from 4-3 and 4-2 from 4-4 yields

$$\text{CO}_2(\text{s}) = \text{CO}_2(\text{g}) \quad (4-5)$$

and

$$\log f_{\text{CO}_2} = \log K_{\text{CO}_2(\text{s})} - \log K_{\text{CO}_2(\text{g})} \quad (4-6)$$

This shows how a fixed fugacity model can be imposed by equilibrium with a fictive solid. A slight rearrangement of equation 4-6 shows how to choose the equilibrium constant for the fictive mineral:

$$\log K_{\text{CO}_2(\text{s})} = \log K_{\text{CO}_2(\text{g})} + \log f_{\text{CO}_2} \quad (4-7)$$

Invocation of this option causes the corresponding gas reaction and its thermodynamic data to be copied into the corresponding mineral data arrays. The log K function is then modified according to equation 4-7.

4.3.6. Changing Temperature and Pressure

The temperature and pressure of most reaction path runs are both constant. However, it is possible to make calculations (in any reaction path mode) in which they vary as a function of reaction progress or time. At the present time, pressure is parameterized as a function of temperature, so it is not yet possible to use EQ6 to calculate models in which these functions vary independently. The means of executing this type of option are described elsewhere in this report (See Section 3.3.4, especially equation 3-37, and Chapter 5). This is a particularly useful option to use in conjunction with the fluid-centered flow-through system mode of calculation (NMODL1 = 3). This combination permits calculation of consequences of heating and cooling as a packet of water moves through a pipe, fracture, or other medium.

5. THE EQ6 INPUT FILE: SETTING UP THE PROBLEM

5.1. INTRODUCTION

The EQ6 INPUT file permits the user to specify a given "single point" thermodynamic calculation or a given reaction path computation. As noted earlier, the user must run EQ3NR (Wolery, 1983) to initialize an EQ6 calculation. The first part of a new INPUT file is created by the user. The PICKUP file generated by EQ3NR is usually appended to this, forming the second part. It is possible (using the IFILE parameter, see below) for EQ6 to read the EQ3NR PICKUP file as a separate file.

The first part of the INPUT file contains text documenting the problem at hand (the thirty lines of text in UTITL1, see below), choices regarding the nature of the calculation (e.g., closed vs. open system; kinetic vs. non-kinetic; etc.), specification of irreversible reactions and corresponding reactants, parameters controlling the rates of these reactions, parameters determining the temperature and pressure, and the print and debugging options. The tolerance and setscrew parameters used in handling the numerical aspects of the calculation also appear here, but users should ordinarily leave these inputs blank and thus take the default values.

The best way to create this part of a new INPUT file is to use the corresponding part of an existing file as a template. This is a highly efficient approach if the user has access to a cursor-editing capability. Such a capability is offered by the "VW" command under the text editor TRIX AC for HP2645A terminals at Lawrence Livermore National Laboratory.

The second part of the EQ6 INPUT file is mostly a compact description of an aqueous system. When EQ3NR writes this part (as the file named PICKUP), this system consists of only the initial aqueous phase. When EQ6 itself writes this part in the course of creating its own PICKUP file (to be used as

INPUT file to use constant fugacity option.
an INPUT file for a subsequent run), this system also includes phases that have precipitated and are in solubility equilibrium with the aqueous phase.

In normal usage, users will not alter the contents of this part of the INPUT file. However, the alter/suppress options (see NXMOD, below) form a general exception to this rule. These options permit suppressing the formation of individually selected species, or changing the equilibrium constants that determine their formation. The formation of species may also be suppressed using subset-selection options (See NXOPT, below) that appear on the first part of the INPUT file.

The INPUT file is read by subroutine READZ. This routine is extensively documented internally by means of comment lines. This internal documentation is the final authority on the EQ6 INPUT file. The user should be aware that the descriptive material on the INPUT file that follows in this section could be out-of-date for the version of EQ6 being used. Appendix H in Wolery (1983) describes the system for naming and identifying versions of the codes and data bases in the EQ3/6 package.

Subroutine READZ writes an "instant" echo of the INPUT file on the OUTPUT file. That is to say, after READZ reads a line or closely related group of lines, it echoes their contents. This helps to identify the sources of read format errors, which most commonly occur when a line is missing from the INPUT file or is out of sequence. The number of lines in the EQ6 INPUT file is variable in both the first and second parts. The appearance of some potential lines depends upon the contents of preceding lines.

As is the case with EQ3NR, there are no species index numbers for users to struggle with in setting up or interpreting the EQ6 INPUT file. All such indexing is internal to the code and is set up at run time. Users deal with species in terms of their names, which are alphanumeric strings. Names are much easier to remember and much more recognizable. However, the names given by the user on the INPUT file must match exactly with those on the supporting data files DATA2 and DATA3 or EQ6 will not recognize them. In such cases the

code will write appropriate diagnostics on the OUTPUT file and terminate execution of the current problem.

It is possible to stack more than one problem on a given INPUT file, so that the code will read one problem, solve it, read another, and so on. If each problem is a "single point" thermodynamic calculation, this practice may be convenient. However, it is generally prudent not to stack reaction path problems in this manner. In fact, a single long problem is best run in several short segments (three to four). EQ6 writes its own PICKUP file, which is an INPUT file for the next run segment. This facilitates the practice of breaking up long calculations.

Segmenting long calculations is desirable because the user can more efficiently check the consequences of assumptions made in defining the problem. It may be desirable or necessary to change the assumptions once the consequences are known and do the calculation over again. Such recalculation is likely to be necessary when trying to model a rock/water interactions experiment or results of a field study.

5.2. INPUT FILE SUMMARY

A summary of the contents of the EQ6 INPUT file and its format is given in Table 1. Parameters for which default values are strongly 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 these pages and keep copies near a computer terminal or card punch for ready reference.

Following the summary is a description of the INPUT file parameters themselves (Table 2). Some of these may not appear on specific examples of INPUT files, depending on the inputs specified for other parameters that precede them. Default values are recommended for all of the numeric control parameters (the tolerance and setscrew parameters).

Examples of EQ6 INPUT files are presented in Chapter 6. The writer suggests that the reader study these in conjunction with the material presented in Tables 1 and 2. The EQ6 INPUT file is fairly lengthy, and it does take some work to learn how to use it. However, in compensation, EQ6 does offer a lot of flexibility by combining many options in one code.

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Table 1. Summary of the EQ6 INPUT File

UPPER PART

<u>Parameters</u>	<u>Format</u>
UTITL1	(15A6)
NMODL1, NMODL2	(12X, I2, 22X, I2)
TEMPCO, JTEMP	(12X, E12.5, 12X, I2)
TK1, TK2, TK3	(3(12X, E12.5))
ZISTR1, ZIMAX	(2(12X, E12.5))
TSTR1, TIMEMX	(2(12X, E12.5))
KSTPMX, CPLIM	(12X, I12, 12X, E12.5)
DZPRNT, DZPRLG, KSPPMX	(2(12X, E12.5), 12X, I5)
IFILE	(12X, I2)
IOPT1, ... , IOPT12	(12X, 10I5)
IOPR1, ... , IOPR10	(12X, 10I5)
IODB1, ... , IODB11	(12X, 10I5)
NXOPT	(12X, I2)
Do N from 1 to NXOPT: UXOPT(N), (UXCAT(J,N), J=1,2)	(12X, A6, 1X, 2A6)
NXOPEX	(12X, I2)
Do N from 1 to NXOPEX: (UXOPEX(J,N), J=1,2)	(12X, 2A6)
NRCT	(12X, I2)
Do NRC from 1 to NRCT: (UREAC(J,NRC), J=1,3) JCODE(NRC), JREAC(NRC) MORR(NRC) MODR(NRC)	(12X, 3A6) (12X, I2, 10X, I2) (2(12X, E12.5))
If JCODE = 1 do I from 1 to IKTMAX, stopping after UENDB(J,I,NXR) = "ENDIT." (NXR indexes reactants that are solid solutions): (UENDB(J,I,NXR), J=1,3), RXBARB(I,NXR)	(3X, 3A6, 3X, E12.5)
If JCODE = 2: VREAC(NRC)	(12X, E12.5)
Do NCB = from 1 to NCTMAX, stopping after UESRB(NCB,NSRT) = "ENDIT." (NSRT indexes reactants that are "special" reactants): UESRB(NCB,NSRT), CESRB(NCB,NSRT)	(3X, A6, 3X, E12.5)
NSK(NRC), SK(NRC), FK(NRC)	(12X, I2, 10X, E12.5, 12X, E12.5)
NRK(NRC)	(12X, I2)

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Table 1. (Continued)

<u>Parameters</u>	<u>Format</u>
If NRK = 0: RK1(NRC), RK2(NRC), RK3(NRC)	(3(12X,E12.5))
If NRK = 1: IMECH(NRC)	(12X,I2)
Do I from 1 to IMECH: RK1(I,NRC), NDACT(I,NRC), CSIGMA(I,NRC)	(12X,E12.5,12X,I2,22X,E12.5)
Do N from 1 to NDACT: UDAC(N,I,NRC), CDAC(N,I,NRC)	(12X,A6,18X,E12.5)
If NRK = 2: RK1(NRC), RK2(NRC)	(2(12X,E12.5))
If NRK = 3: RK1(NRC), RK2(NRC), RK3(NRC)	(3(12X,E12.5))
DLZIDP(*)	(12X,E12.5)
TOLBT(*), TOLDL(*), TOLX(*)	(3(12X,E12.5))
TOLSAT(*), TOLSST(*)	(2(12X,E12.5))
SCREW1(*), SCREW2(*), SCREW3(*)	(3(12X,E12.5))
SCREW4(*), SCREW5(*)	(2(12X,E12.5))
ZKLOGU(*), ZKLOGL(*)	(2(12X,E12.5))
DLZMX1(*), DLZMX2(*)	(2(12X,E12.5))
LOWER PART	
UTITL2	(15A6)
UACION	(12X,2A6)
TEMPCI	(12X,E12.5)
NXMOD	(12X,I2)
Do N from 1 to NXMOD: (UXMOD(J,N), J=1,3)	(12X,3A6)
JXMOD(N), KXMOD(N), XLKMOD(N)	(12X,I2,22X,I2,22X,E12.5)
NFFG	(12X,I2)
Do N from 1 to NFFG: (UFFG(J,N), J=1,2), MOFFG(N), XLKFFG(N)	(12X,2A6,12X,E12.5,12X,E12.5)

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

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Table 1. (Continued)

<u>Parameters</u>	<u>Format</u>
IOPG1, ..., IOPG6	(12X,I2,22X,I2,22X,I2)
KCT, KSQ, KGMT	(12X,I2,22X,I2,22X,I2)
KMT, KXT, KDIM	(12X,I2,22X,I2,22X,I2)
KPRS	(12X,I2)
Do KC from 1 to KCT: UELEMB(KC), MTEB(KC)	(3X,A6,9X,E25.15)
ELECTR	(18X,E25.15)
Do KCOL from 1 to KDIM: (UNRMS(I,KCOL), I=1,2), (UNDIS(I,KCOL), I=1,2), ZLGI(KCOL,1)	(3X,2A6,3X,2A6,3X,E25.15)
If KPRS = 0 stop, else:	
Do N from 1 until UPRMN(1,N) = "ENDIT": (UPRMN(J,N), J=1,2), MPRMB(N)	(3X,2A6,3X,E25.15)
Do N from 1 until UPRXX(1,N) = "ENDIT": (UPRXX(J,N), J=1,2)	(3X,2A6)
Do I from 1 until UPRMX(1,N) = "ENDIT": (UPRMX(J,I), J=1,2), MPRMB(N)	(3X,2A6,3X,E25.15)

Table 2. EQ6 INPUT File Parameters

UTITL1	Thirty lines of text that describe the input problem.
NMODL1	Physical model option switch. = 0 Compute the state of the system at the start of the reaction path and stop. = 1 Titration. = 2 Closed system. = 3 Flow-through open system (follows a packet of flowing fluid, see text).
NMODL2	"Economy" reaction path option switch = 0 "Economy" mode not selected = 1 "Economy" calculational mode activated (if IOPT1 = 0 and NMODL1 = 1 or 2)
TEMPCO	Temperature (°C) at the start of the run or run segment.
JTEMP	Temperature variance option switch. = 0 $TEMPC = TEMPCO + TK1*Z11 + (1/2)*TK2*Z11**2 + (1/3!)*TK3*Z11**3$; Z11 is the overall value of reaction progress. TEMPC = TEMPCO if TK1 = TK2 = TK3 = 1 $TEMPC = TEMPCO + TK1*TIME + (1/2)*TK2*TIME**2 + (1/3!)*TK3*TIME**3$ = 2 $TEMPC = (TEMPCO*TK1 + TK2*Z11)/(TK1 + Z11)$ This is an equation for mixing two waters of different temperatures, see text.
TK1, TK2, TK3	Temperature variance coefficients, see above.
ZISTR1	The value of the overall reaction progress parameter (Z11) at the start of the run or run segment.
ZIMAX	The maximum allowed value of Z11 for a run segment (see text).
TSTRT	The value of time (sec) at the start of a run segment.
TIMEMX	The maximum allowed value of time (sec) for a run segment.
KSTPMX	The maximum allowed number of reaction progress or time steps for a run segment (see text).
CPLIM	The maximum allowed number of computing units for a run segment (see text).

Table 2 (Continued)

DZPRNT	Linear print interval (in terms of reaction progress). The default is pseudo-infinite, which turns off the linear print interval feature.
DZPRLG	Logarithmic print interval (in terms of reaction progress). The default is 0.5. Other good values would be 0.25 and 1.0. The logarithmic print interval is generally more useful than the linear one.
KSPPMX	Maximum number of steps since the last point of a full printout of the state of the system. Such a printout is caused whenever this limit is reached.
IFILE	Unit number of the file the last part of the problem input data. = 60 Read from file named INPUT. This is also the default. = 8 Read from the file named PICKUP.
IOPT1	Kinetic mode option. = 0 Reaction progress mode (no time frame). NRK must be zero for all reactants. = 1 Reaction-progress/time mode (real kinetics). This option is required to run with real kinetic rate laws (NRK greater than zero).
IOPT2	Phase boundary search option. = 0 The step size is constrained by the predicted locations of phase boundaries. IOPT1 = 1 forces IOPT2 = 0. So does NMODL1 = 3. = 1 Phase boundary locations are predicted and printed on the OUTPUT file, but do not constrain the step size. Not permitted if NMODL2 = 1. = 2 Calculations to predict the locations of phase boundaries are not made.
IOPT3	Interfacing I/O option. = -1 No PICKUP file is written. = 0 EQ6 writes a PICKUP file. = 1 EQ6 writes a sequence of PICKUP files, each corresponding to a print point.
IOPT4	Solid solution option. = 0 Solid solutions are ignored. = 1 Solid solutions may appear as reactants and as secondary minerals.

Table 2. (Continued)

IOPT5	Option to eliminate secondary phases at the start of a run by transferring masses to the physically removed subsystem. = 0 No transfer takes place. = 1 Secondary phases are reduced to trivial masses. = 2 Secondary phases are entirely wiped out. = 3 Secondary phases are wiped out and precipitation of all such phases is suppressed for the remainder of the run segment.
IOPT6	Option to clear the physically removed subsystem before the first step of reaction progress. = 0 The option is not taken. = 1 This option is done.
IOPT7	Option switch, not currently used.
IOPT8	Option switch, not currently used.
IOPT9	Option switch, not currently used.
IOPT10	Option for calculating the state of the system at the start of the run. = 0 The state of the initial system given on the lower part of the INPUT file is recalculated (EQ6 does not accept this information at face value). = 1 The state of the initial system is accepted as-is. EQ6 may reset IOPT10 to 1 and try again if it runs into trouble at the start of a run segment.
IOPT11	Option switch, not currently used.
IOPT12	Option switch, not currently used.
IOPR1	Option to print the species loaded and not loaded from DATA2 and DATA3. = -1 Does not print. = 0 Does not print. = 1 Prints.
IOPR2	Print option, not currently used.
IOPR3	Option to print all species loaded into memory and their associated log K values, if any. = -1 Does not print. = 0 Does not print. = 1 Prints.

Table 2. (Continued)

- IOPR4 Option to print the aqueous species distribution at each print point.
 = -1 Does not print.
 = 0 Prints species whose concentrations are not less than 1×10^{-12} molal.
 = 1 Prints all aqueous species in the model.
- IOPR5 Option to print ionic activity ratios at each print point.
 = -1 Does not print.
 = 0 Does not print.
 = 1 Prints.
- IOPR6 Option to print the bulk oxide composition of the theoretical mineral assemblage at each print point.
 = -1 does not print.
 = 0 does not print.
 = 1 prints.
- IOPR7 Option to print mineral saturation indices at each print point.
 = -1 Does not print.
 = 0 Prints for those minerals not undersaturated by more than 10 kcal.
 = 1 Prints for all minerals.
- IOPR8 Option to print equilibrium gas fugacities.
 = 0 Does not print.
 = 1 Prints the fugacities.
- IOPR9 Option to print, not currently used.
- IOPR10 Option to print, not currently used.
- IODB1 Option to print general diagnostic debugging messages.
 = 0 Does nothing.
 = 1 Prints level 1 diagnostics.
 = 2 Prints level 2 diagnostics.
- IODB2 Option to print debugging messages when reading the data files DATA2 and DATA3.
 = 0 Does nothing.
 = 1 Prints a summary of diagnostic information.
 = 2 Prints detailed diagnostics.
- IODB3 Option to print step size and order selection diagnostics.
 = 0 Does nothing.
 = 1 Prints the orders being considered and their corresponding step size scaling factors.

Table 2. (Continued)

- I0DB4 Option to print debugging messages concerning Newton-Raphson iteration in the NEWTON subroutine.
 = 0 Does nothing.
 = 1 Prints summary diagnostics.
 = 2 Prints detailed diagnostics.
- I0DB5 Option to print debugging messages concerning phase boundary searches.
 = 0 Does nothing.
 = 1 Prints details of the phase boundary searches.
- I0DB6 Option to print debugging messages concerning iteration to calculate the saturation indices of solid solutions that are not already product phases.
 = 0 Does nothing.
 = 1 Prints details of the calculations.
- I0DB7 Option to print diagnostics to verify proper operation of the NMODL = 3 option (see above).
 = 0 Does nothing.
 = 1 Prints at each print point the values of the master variables and their derivatives with respect to the overall reaction progress variable.
- I0DB8 Option to provide special control of the I0DB3 and I0DB7 options.
 = 0 Does nothing.
 = 1 Turns these options on when DELZI (the step size in terms of reaction progress) is less than or equal to DLZMX1 (see above) and turns them off after DELZI increases.
- I0DB9 Option to print diagnostic messages pertaining to the kinetic mode (IOPT1 = 1, see above).
 = 0 Does nothing.
 = 1 Prints level 1 kinetics diagnostics.
 = 2 Prints level 2 kinetics diagnostics.
- I0DB10 Option to check the consistency of finite-difference and truncated Taylor's series expressions for the master system variables as functions of the reaction progress parameter.
 = 0 Does nothing.
 = 1 Prints values of the I0DB10-th master variable calculated by both types of expressions.

Table 2. (Continued)

I0DB11	Option to check the consistency of finite-difference and truncated Taylor's series expressions for reaction rates as functions of the reaction progress parameter. = 0 Does nothing. = 1 Prints values of the I0DB11-th reaction rate calculated by both types of expressions.
NXOPT	The number of subset-selection precipitation suppression options to follow (see text). These options suppress precipitation of pure minerals. Compare the alter/suppress options for individual minerals using NXMOD (see below).
UXOPT	A six-character alphanumeric string denoting a type of subset-selection precipitation suppression option. These are: ALL = Suppress precipitation of all pure minerals. ALWITH = Suppress all solids composed of a specified chemical element (e.g., "ALWITH MG").
UXCAT	The name of a chemical element given with a UXOPT input.
NXOPEX	The number of exceptions to the subset-selection precipitation suppression options.
UXOPEX	A twelve-character alphanumeric string that is the name of a mineral not to be suppressed by any of the subset-selection options. This input does not override the alter/suppress options (see below).
NRCT	The number of reactants to follow.
UREAC	The name of a reactant.
JCODE	The species type of a reactant. = 0 Mineral. = 1 Solid solution. = 2 "Special" reactant. A "special" reactant is a species that is not on the supporting data files. = 3 Aqueous species. = 4 Gas.

Table 2. (Continued)

JREAC	Status switch for a reactant. = 0 Set to react. This is the only value that users should enter. Other values may be written by EQ6 on the PICKUP file. = -1 The reactant has saturated the aqueous solution, but some reactant mass remains and continues to react irreversibly. A product mass of the same species may also exist. = 1 The reactant mass has been exhausted. = 2 The reactant has saturated the aqueous solution, and any remaining reactant mass has been transferred to product mineral status.
MORR	Moles of reactant remaining. This is the starting reactant mass when making up a new INPUT file.
MODR	Moles of reactant that have been destroyed. Users should normally leave this input blank.
UENDB	Name of a pure mineral end-member of a solid-solution reactant.
RXBARB	The mole fraction of said end-member mineral in a solid-solution reactant.
VREAC	The molar volume of a reactant. Users should normally enter a value only for "special" reactants that are solids.
UESRB	The name of a chemical element that makes up a "special" reactant.
CESRB	The number of moles of said chemical element per mole of "special" reactant.
NSK	Reactant surface area option switch. = 0 Constant surface area. = 1 Constant specific surface area.
SK	Surface area of a reactant, cm ² . This defaults to 100 cm ² if left blank. The surface area of a reactant is meaningful only if it appears in a kinetic rate law.
FK	Ratio of effective surface area to actual surface area of a reactant. This is a kinetic fudge factor. It defaults to a value of unity if left blank.

Table 2. (Continued)

NRK

Rate law code.

- = 0 Arbitrary relative rate law (equation 3-33). This defines the relative rate (RRELRC) by a second-order truncated Taylor's series in reaction progress (Z11):

$$RRELRC = RK(1) + RK(2)*Z11 + 0.5*RK(3)*Z11**2.$$

The last two terms are an embellishment that is rarely used. This is the only rate law that can be used without setting IOPT1 to 1.

- = 1 Transition theory rate law (equation 3-34) defining the actual rate of reaction (RREAC, mol/sec), and allowing the use of up to three terms to describe parallel mechanisms:

$$RREAC = FK*SK* \sum_{I=1}^{IMECH} RK(I)*EXP[-AFF/(CSIGMA(I)*RCONST*TEMPK)]$$

where

FK is a surface area fudge factor,

SK is surface area (cm²),

RK is the rate constant (mol/cm²-sec),

AFF is the affinity,

CSIGMA is the ratio of the macroscopic and microscopic affinities (nearly always unity),

RCONST is the gas constant, and

TEMPK is the absolute temperature.

- = 2 Affinity-to-a-power rate law (equation 3-35):

$$RREAC = FK*SK*RK(1)*AFF**RK(2)$$

where

FK is a surface area fudge factor,

SK is surface area (cm²),

RK(1) is the rate constant (mol/cm²-sec),

AFF is the affinity, and

RK(2) is the exponent of the affinity.

- = 3 Two-term linear-parabolic rate law (equation 3-36):

$$RREAC = FK*SK*(RK(1) + RK(2)*[TIME - RK(3)]**0.5)$$

Table 2. (Continued)

where

FK is a surface area fudge factor,

SK is surface area (cm^2),

RK(1) is the linear rate constant ($\text{mol}/\text{cm}^2\text{-sec}$),

RK(2) is the parabolic rate constant

($\text{mol}/\text{cm}\text{-sec}^{1/2}$),

TIME is the time (sec), and

RK(3) is the time (usually zero) when reaction begins.

- DLZIDP Dump interval, an upper limit on the interval of reaction progress in which product minerals remain in contact with the water before most of their masses are removed. This parameter is relevant only to the flow-through open system model which follows a particular packet of water (NMODL1 = 3). The default is pseudo-infinite. This suffices for runs in which all product phases are pure minerals (another mechanism guards against re-dissolution of these phases). DLZDP should be set to about 1/10 or so of the expected final value of reaction progress when there are solid-solution product phases in the model.
- TOLBT Convergence tolerance on Newton-Raphson residual functions.
- TOLDL Convergence tolerance on Newton-Raphson correction terms.
- TOLX Convergence tolerance for search/find routines.
- TOLSAT Supersaturation tolerance which the affinity must exceed before EQ6 will attempt to precipitate a phase. A good value is 0.0001 (kcal). Smaller values may result in disaster.
- TOLSST Supersaturation step-size cut parameter. The step size is cut when the affinity to precipitate of a non-suppressed phase exceeds this limit.
- SCREW1 Step-size control parameter that bounds the magnitude of the highest order term in a Taylor's series for a master variable.
- SCREW2 Maximum value of BETAMX (largest residual function magnitude) prior to Newton-Raphson iteration at which EQ6 will not try to cut the step size.

Table 2. (Continued)

SCREW3	Step-size control parameter similar to SCREW1. It bounds the magnitude of the highest order term in a Taylor's series for a rate function. It operates under IOPT1 = 1 only. It also serves a function similar to that of SCREW4 in testing the estimated error in the time (see below).
SCREW4	Tolerance on the difference between actual and predicted rate functions. If both the SCREW4 test and the analogous test with SCREW3 are not satisfied, the code either cuts the step size or initiates corrector iteration.
SCREW5	Under-relaxation parameter that bounds the magnitude of a Newton-Raphson iteration correction term.
ZKLOGU	Threshold and/or target value for the log mass of non-aqueous phases. It is used in several ways. (1) When the log mass of a phase is less than this value, EQ6 will not limit the step size to keep the corresponding Taylor's series within the normal accuracy limit. (2) ZKLOGU is the target mass used when trying to estimate from Taylor's series when the phase will disappear. (3) It is also defines the maximum mass of a phase which the user is willing to let re-dissolve in the flow-through system model (NMODL1 = 3).
ZKLOGL	Amount by which the log mass of a phase in the equilibrium subsystem is decremented by a transfer to the physically removed subsystem under NMODL1 = 3.
DLZMX1	Step size when the order of the Taylor's series (NORD) is zero.
DLZMX2	Upper limit on the step size when the order is greater than zero. The default is quasi-infinite.

Table 2. (Continued)

UTITL2	Thirty lines of text from the previous EQ3NR or EQ6 run.
UACION	Name of the ion, if any, that defines the equivalent stoichiometric ionic strength. This must be "NA+", "CL-", or blank.
TEMPCI	The temperature at the end of the previous EQ3NR or EQ6 run. This parameter is informational in nature.
NX:MOD	Number of suppressed/alterred species/reaction pairs that follow.
UXMOD	Name of a species to be suppressed or 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 The species is suppressed. No XLKMOD input is required. = 0 The log K value from the data file is replaced by XLKMOD. = 1 The log K value is augmented by XLKMOD. = 2 Same as KXMOD = 1, but XLKMOD is in kcal/mol.
XLKMOD	Corresponding equilibrium constant alteration function whose meaning is determined by KXMOD.
NFFG	The number of gas species whose fugacities are to be fixed.
UFFG	The name of a gas species whose fugacity is to be fixed.
MOFFG	The amount, if any, of such a gas species, in moles, to be added to the system at the start of the run.
XLKFFG	The logarithm of the desired fixed fugacity.

Table 2. (Continued)

IOPG1	Activity coefficient equation option switch = -3 Short form of hydration theory equations (Wolery, 1984) = -2 Short form of the Helgeson et al. (1981) equations = -1 The Davies (1962) equation, with a thermodynamically consistent equation for the activity of water = 0 The B-dot equation (Helgeson, 1969) for ionic species, unit activity coefficient for polar neutral species, the activity coefficient of aqueous CO ₂ for nonpolar neutral species, and the expression of Helgeson et al. (1970) for the activity of water. = 1 Pitzer's (1973, 1975) equations = 2 Long form of hydration theory equations (Wolery, 1984)
IOPG2	Activity coefficient option switch = 0 The function J(x), which appears in Pitzer's (1975) higher order electrostatic term, is estimated by the method of Harvie and Weare (1980) = 1 The function J(x) is estimated by the approximation of Pitzer (1975)
IOPG3	Activity coefficient option switch, not currently used
IOPG4	Activity coefficient option switch, not currently used
IOPG5	Activity coefficient option switch, not currently used
IOPG6	Activity coefficient option switch, not currently used
KCT	Number of chemical elements in the model.
KSQ	Number of active master species in the model
KGMT	Position of the last activity coefficient variable in the INDEX array
KMT	Last pure mineral entry in the INDEX array.
KXT	Last solid solution entry in the INDEX array.
KDIM	Last entry in the INDEX array. KDIM is equivalent to the number of master variables.

Table 2. (Continued)

KPRS	Flag denoting whether or not mineral masses in the physically removed subsystem are appended to this INPUT file. = 0 No such data are appended. = 1 Such data are appended.
UELEMB	Name of a chemical element in the model.
MTEB	Moles of said element in the equilibrium subsystem.
ELECTR	Electrical imbalance (in equivalents).
UNRMS	Name of a master variable species, aqueous or mineral.
UNDMS	Name of an aqueous master species on the data file that is to be switched with that given by the corresponding UNRMS input. UNDMS should be blank if UNRMS does not refer to an aqueous species.
ZLGI	The value of a master variable function.
UPRMNB	Name of a pure mineral in the physically removed subsystem.
MP ^o MNB	Moles of said pure mineral in that subsystem.
UPRXX	Name of a solid solution in the physically removed subsystem.
UPRMX	Name of an end-member of said solid solution.
MPRMXB	Moles of said end-member of said solid solution.

5.3. SOME FURTHER DISCUSSION

Many of the important points about INPUT file parameters have been discussed sufficiently earlier in this report (especially in Chapter 4). A few points remain to be covered, however. These will be discussed in this section.

The INPUT file begins with thirty lines of text (UTITL1). The purpose of this text is to provide an abbreviated description of the problem being run. Additional information may be incorporated into the INPUT file by means of comment lines. These are marked by an asterisk in column one, and are analogous to the comment lines in FORTRAN source codes. They may appear anywhere in the INPUT file. However, these lines are not echoed on the OUTPUT file.

EQ6 will stop if a reaction path has reached a point of overall thermodynamic equilibrium. This occurs in the closed or flow-through open system models when all reactants are either exhausted or have saturated the water. However, the INPUT file also provides several arbitrary controls on the length of a run segment. ZIMAX is an upper limit on the value of the overall reaction progress parameter, ZI1. This limit will be located exactly if ZI1 would otherwise exceed it. TIMEMX is an upper limit on time (in seconds). It is not located exactly, but the code (when operating in the kinetic mode) will stop after the first step which exceeds this limit. KSTPMX is the maximum allowed number of steps in the run segment and perhaps offers the easiest way for the user to control the length of a run. As noted earlier, a "single point" thermodynamic calculation is carried out by setting KSTPMX = 0.

CPLIM is a limit on the number of computing units used. A computing unit is an administrative measure of the usage of a computer, and is installation dependent. The CPLIM feature is not active in the LLNL version of EQ6. It should be enabled locally at installations at which the

consequence of exceeding the predetermined limit on computing units (usually specified on a job card or job line) is catastrophic termination. This results in no PICKUP file being generated. A call to a local system routine must be provided to return the number of computing units used. Several commented-out examples are given in the EQ6 source code. The value of CPLIM should be sufficiently less than the actual administrative limit for EQ6 to write a PICKUP file and terminate before catastrophic termination occurs.

EQ6 does not print the state of the geochemical system being modeled at every step of reaction progress. It does give such a print when a significant event occurs, such as the precipitation of a new secondary phase or the point of exhaustion of a reactant phase. Apart from these kinds of print points, the user may specify three kinds of print intervals, one (DZIPR) linear in reaction progress, the second (DZPRLG) logarithmic in reaction progress, and the third (KSPPMX) defined in terms of the number of steps since the last print point. The print points generated by the first two of these variables are independent of the occurrence of the other kinds of print points mentioned above. The logarithmic print interval usually provides the best spacing of detailed information. A too-small value of the linear print interval could produce a lot of not very useful printout. Consequently, the default value for the linear print interval is pseudo-infinite, which turns off this print control mechanism. Good values for the logarithmic print interval are 0.25, 0.50, or 1.0. The default is 0.5. The default for KSPPMX is 25.

There are three general option switch arrays. The IOPT switches (IOPT1, IOPT2, IOPT3, etc.) are model option switches. The IOPR switches (IOPR1, IOPR2, IOPR3, etc.) are print option switches, and the IODB switches (IODB1, IODB2, IODB3, etc.) are debugging print options. The usage of these switches is given in detail in Table 2. Note that IOPT1 is particularly important, because it determines whether the code runs in ordinary reaction-progress mode (IOPT1 = 0) or kinetic reaction-progress mode (IOPT1 = 1). The IODB switches should all be set to zero, except in debugging runs.

The activity coefficient options are specified on the second half of the INPUT file by the IOPG option switches (IOPG1, IOPG2, IOPG3, etc.). The

user should make the desired selections in the initializing EQ3NR run. It is not advisable under most circumstances to later change these options without going back to EQ3NR and repeating the initializing calculation.

Much of the work in intelligent reaction-path modeling involves deciding which secondary phases will be allowed to precipitate. The EQ6 code itself can decide if a given phase must precipitate in order to avoid supersaturating the aqueous solution. The code does not know, however, whether it would make more sense, geochemically speaking, to precipitate the phase or to allow the supersaturation. The default condition is that EQ6 will precipitate the phase. Every mineral read from those on the data file is a potential candidate. The user, however, can specify that precipitation of certain phases is to be suppressed. There are two methods of doing this on the INPUT file.

The first method is to use the subset-selection suppression options for pure minerals. NXOPT is the number of such options given on the file. The two options, entered as UXOPT(N), N=1,NXOPT, are "ALL" and "ALWITH". If "ALL" is used, NXOPT should be 1 and no "ALWITH" options should appear. Each "ALWITH" option requires a separate entry, and must be followed by an argument (UXCAT(N)) that is the symbol of a chemical element on the data file. Under "ALL", all pure minerals are suppressed. Under "ALWITH", those minerals containing the specified elements are suppressed.

Exceptions to the "ALL" and "ALWITH" suppression options may also be specified. NXOPEX is the number of exceptions. The names of the exceptions are entered as UXOPEX(J,N), J=1,2, N=1,NXOPEX. Thus, to allow only amorphous silica, kaolinite, and amorphous Fe(OH)₃ as potential precipitates, one would specify on the INPUT file:

```
NXOPT= 1
UXOPT= ALL
NXOPEX= 3
UXOPEX= AMORPHOUS SILICA
UXOPEX= KAOLINITE
UXOPEX= AMORPHOUS FE(OH)3
```

2 6 mins to not sup. (is, allow to not)

} not suppress

Note that this situation is the complement of the normal one where every mineral read from the data base is allowed to precipitate. To suppress precipitation of all potassium and magnesium minerals, except K-feldspar, illite, and sepiolite, specify:

```
NXOPT= 2
UXOPT= ALWITH K
UXOPT= ALWITH MG
NXOPEX= 3
UXOPEX= K-FELDSPAR
UXOPEX= MUSCOVITE
UXOPEX= SEPIOLITE
```

The alter/suppress functions (using the parameters NXMOD, UXMOD, JXMOD, KXMOD, and XLKMOD), described sufficient detail earlier in this section, permit suppression of individually named minerals. More generally, they permit either suppression of a given species (aqueous species, pure mineral, gas, or solid solution) or, for aqueous species, pure minerals, and gases, changes in the associated equilibrium constants. They are also in the EQ3NR code (where they are relevant only in the case of aqueous species), and are passed on to EQ6 through the PICKUP file. The material in this section of the EQ6 INPUT file is written by a code (EQ3NR or EQ6 itself) to be read by a code (EQ6). The alter/suppress options are the only part of the lower half of the EQ6 INPUT file that the user should modify in normal use.

The other major block of input the user must provide on the INPUT file defines the reactant phases and how they react irreversibly in an aqueous geochemical system. NCRT is the number of reactants so defined. This number may be zero, for example, if the user wants to calculate the consequences of heating or cooling an aqueous solution. If it is not zero, a sequence of input blocks follow, one per reactant.

A reactant input block begins with the name of a reactant (UREAC(J,NRC), where NRC denotes the NRC-th reactant on the INPUT file). This is followed by a species type code, JCODE(NRC), which has the following meanings:

- 0 Pure mineral.
- 1 Solid solution.
- 2 "Special" reactant.
- 3 Aqueous species.
- 4 Gas species.

A "special" reactant is a species that is not on the supporting thermodynamic data base. It could actually be a pure mineral, for instance. A whole rock is one example of a "special reactant" (oceanic basalt was treated this way by Wolery, 1978). Also, a second aqueous solution in a fluid-mixing scenario is another example.. JREAC(NRC) is a status code. The user should leave this input blank when preparing an EQ6 INPUT file, and not tamper with values that EQ6 writes on PICKUP files. MORR(NRC) is the mass of the reactant, in moles. If the reactant is a whole rock or second aqueous solution special reactant, it is convenient to define a "mole" as a 1 kg mass. MODR(NRC) is the number of moles of the reactant that have been destroyed. The user should leave this input blank when making up a new INPUT file, and normally should not change the EQ6-written MORR and MODR values on a PICKUP file.

If the reactant is a solid solution, the names of the pure mineral end-members (UENDB(J,NXR), J=1,2, for the NXR-th reactant that is a solid solution) must follow, along with the corresponding mole fractions. These will be normalized if they do not sum to unity. If the reactant is a special reactant, a value for the volume (cm^3) of one mole of substance under the conditions of the run (VREAC(NRC)) may be entered, followed by the symbol for each chemical element (UESRB(NCB,NSR), where the reactant is the NSR-th special reactant) and the corresponding number of moles of the element per mole of special reactant. For special reactants that are whole rocks or aqueous solutions, we recommend equating one "mole" with a mass of 1 kg.

The surface area of a reactant is read in as SK(NRC). This is given in units of square centimeters. It is the absolute surface area, not the specific surface area, which might have units of cm^2/mol or cm^2/g . The surface area may or may not actually be used in the calculations, depending on the rate options selected. There are currently two possible treatments, determined by the reactant surface area code NSK(NRC):

- 0 Constant surface area.
- 1 Surface area changes in proportion to the reactant mass.

The default for SK(NRC) is 100 cm^2 . FK(NRC) is a fudge factor equal to the ratio of kinetically effective surface area to total surface area. It is used in the calculations only when SK(NRC) is used. Its default value is unity.

The parameter NRK(NRC) is the rate law code. The various existing options have been described earlier. They include:

- 0 Relative rate input (arbitrary kinetics).
- 1 Transition-state theory rate law.
- 2 Affinity-to-a-power rate law.
- 3 Linear-plus-parabolic rate law.

The option NRK = 0 is the only one allowed if IOPT1 = 0 (arbitrary kinetics mode). Under this option the relative rate is either constant or a function of the overall reaction progress variable (Z11). Kinetic rate laws in addition to the ones listed above can be added by defining new NRK options in subroutine REACTS and making necessary additions to subroutine READZ, which reads the INPUT file, and subroutine SCRIBE, which writes the PICKUP file.

6. SAMPLE PROBLEMS: INPUTS AND OUTPUTS

6.1. INTRODUCTION

This chapter presents four examples of the usage of EQ6. In all cases, the initializing EQ3NR INPUT files and the EQ6 INPUT files are presented in their entirety. The EQ6 OUTPUT file for the first example is also given in its entirety. Only selected parts of the OUTPUT files will be presented for the other examples. Included with each example is a discussion of the relevant features. Users should compare the sample EQ6 INPUT files with the INPUT file description presented in Chapter 5. For other examples of the usage of EQ6, the reader is directed to Delany and Wolery (1984), Jackson (1984), and other papers and reports cited in Chapter 2.

6.2. "SINGLE POINT" THERMODYNAMIC CALCULATIONS

6.2.1. FINDING AN EQUILIBRIUM SET OF PRECIPITATES FROM MULTIPLY-SUPERSATURATED SEA WATER

Surface sea water at 25°C is supersaturated with respect to a large number of minerals. Figure 6 presents an EQ3NR INPUT file, ISWMJP, for this fluid. Most of the trace constituents have been omitted from this model. This INPUT file is itself a slightly more extended version of the sea water test case, ISWMAJ, presented by Wolery (1983) in the EQ3NR user's guide (See Section 5.2 of that report).

The PICKUP file written by EQ3NR when given the INPUT file ISWMJP composes the lower part of the EQ6 INPUT file ISWEQS, shown in Figure 7. This part begins with the line "* PICKUP FILE WRITTEN BY EQ3NR.3230U52". The upper part

Figure 6. EQ3NR INPUT file, ISWMJP.

INPUT FILE NAME= ISWMJP CREATED= 03/19/84 CREATOR= T.J. VOLERY

SEA WATER TEST CASE, MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON. THIS IS AN EXTENSION OF THE CLASSIC SEA WATER 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.

THERE IS NO FORCED ELECTRICAL BALANCING IN THIS RUN.

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.

TEMPC=	25.	TDSPKG=	0.	TDSPL=	0.
RHO=	1.02336	UREDIX=			
FEP=	0.500	TOLDL=	0.	TOLSAT=	0.
TOLET=	0.				
ITERMX=	0				
IOPT1-10=	-1				
IPRNT1-10=	0				
IDBUG1-10=	0				
UEEAL=		UACION=	CL-		
NXMOD=	1				
SPECIES=	PD-OXYANNITE	OPTION=	-1	XLKMOD=	0.
TYPE=	1				
	NA+		10768.		3
	K+		399.1		3
	CA++		412.3		3
	MG++		1291.8		3
	AL+++		0.002		3
	SiO2(AQ)		4.28		3
	H+		-8.22		16
	HCO3-		.002322		10
	CL-		19353.		3
	SO4--		2712.		3
	FE++		0.002		3
	O2(AQ)		6.6		2
	H2(AQ)				27
	HS-				27
	CO3--				30
HCO3-					
ENDIT.					

Figure 7. EQ6 INPUT file, ISWEQS.

INPUT FILE NAME= ISWEQS REVISED= 8/3/16/84 REVISOR= T.J. WOLERY

THIS IS A SIMPLE THERMODYNAMIC CALCULATION TO DEMONSTRATE EQ6'S ABILITY TO FIND AN EQUILIBRIUM ASSEMBLAGE OF SOLIDS RESULTING FROM PRECIPITATION FROM A SOLUTION THAT IS SUPERSATURATED WITH RESPECT TO A LARGE NUMBER OF MINERALS. THE FLUID HERE IS SEA WATER, REPRESENTED BY MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON.

THE PHASES PRECIPITATED ARE THOSE THAT ARE THE MOST THERMODYNAMICALLY FAVORED, ACCORDING TO THE THERMODYNAMIC DATA BASE. NO PHASES HAVE BEEN SUPPRESSED, WHICH CAN BE DONE USING THE NXOPT OR NXMOD OPTIONS.

THIS RUN ENDS AFTER THE PRECIPITATION CALCULATIONS ARE COMPLETED. NO IRREVERSIBLE REACTIONS ARE SPECIFIED (NRCT=8). ALSO, THE MAXIMUM NUMBER OF REACTION PROGRESS STEPS IS SET TO ZERO (KSPTMX=8).

```

NMODL1= 2
TEMPC8= 25.      JTEMP= 8
TK1= 8.      TK2= 8.      TK3= 8.
Z1STRT= 8.      Z1MAX= 1.
TSTRT= 8.      TIMEMX= 8.
KSTPMX= 8.      CPLIM= 8.
DZ1PR= 1.E+5      DZPRLG= 1.8
IFILE= 68
IOPT1-18= 8 8 8 8 8 8 8 8 8 8 8
11-28= 8 8 8 8 8 8 8 8 8 8 8
IOPR1-18= 8 8 8 8 8 8 8 8 8 8 8
IODB1-18= 8 8 8 8 8 8 8 8 8 8 8
11-28= 8 8
NXOPT= 8
NRCT= 8

```

```

-----
DLZIDP= 8.      TOLDL= 8.      TOLX= 8.
TOLBT= 8.      TOLSST= 8.
TOLSAT= 8.      SCREW2= 8.      SCREW3= 8.
SCREW1= 8.      SCREWS= 8.
SCREW4= 8.      ZKLOGL= 8.
ZKLOGU= 8.      DLZMX2= 8.
DLZMX1= 8.
-----

```

* PICKUP FILE WRITTEN BY EQ3NR.3238U52
* SUPPORTED BY EOLIB.3238U82
INPUT FILE NAME= ISWMJP CREATED= 8/3/19/84 CREATOR= T.J. WOLERY

SEA WATER TEST CASE, MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON. THIS IS AN EXTENSION OF THE CLASSIC SEA WATER MODEL OF

Figure 7. EQ6 INPUT file, ISWEQS (Continued).

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.

THERE IS NO FORCED ELECTRICAL BALANCING IN THIS RUN.

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. 262, 57-66.

```

UACION= CL-
TEMPC1= 2.58888E+01
NXMOD= ?
SPECIES= PD-OXYANNITE
TYPE= 1
NFFG= 8
KCT= 12
KDIM= 15
OPTION= -1
KMT= 15
KPRS= 8
XLKMOD= 8.
KXT= 15

O          5.5629E923446E153E+01
NA         4.683775554589E05E-01
K          1.82E768325745569E-02
CA         1.82869261477E471E-02
MG         5.31495577E417717E-02
AL         7.412348973388611E-08
SI         7.12336E628453687E-05
H          1.11E2E5E66286275E+02
C          2.8958E05E5462143E-03
CL         5.4587764882E251E-01
S          2.823294259718223E-02
FE         3.581212956827398E-08
ELECTR    7.93E1997216E6357E-04
H2O        H2O          1.744365733541414E+00
NA+        NA+         -3.4665142372E7868E-01
K+         K+          -1.998455E2937891E+00
CA++      CA++        -2.8431929E7349521E+00
MG++      MG++        -1.334637711162529E+00
AL+++     AL+++       -1.697853675564238E+01
SiO2(AQ)  SiO2(AQ)      -4.174261919974839E+00
H+        H+           -8.125147876E9E978E+00
HCO3-     CO3--       -2.816E64673883779E+00
CL-       CL-          -2.7289214665E633E-01
SO4--     SO4--        -1.834119181985116E+00
FE++      FE++        -1.346E32643998E6E+01
O2(G)     O2(G)         -1.64299329622E233E+01
XISTEC    -2.629E4694E568411E-01
XI        -1.9327E3469E1915E-01
    
```

was created by text editing. The purpose of this problem is to have EQ6 find an equilibrium set of precipitates. The number of minerals in this set is often considerably smaller than the number of phases for which the water is supersaturated. This example illustrates EQ6's capability to deal with multiply-supersaturated solutions. The time required to run this problem on a CDC 7600 computer was 6.00 seconds (4.96 seconds CPU).

A complete OUTPUT file (OSWEQS) is reproduced in Figure 8. This file begins with an "instant" echo of the INPUT file, as is the case for EQ3NR (Wolery, 1983). This echo is written by subroutine READZ, which reads the INPUT file. The "instant" echo is followed by a few short messages, then by a somewhat lengthy "nice" echo, written by subroutine ECHOZ, which begins with "EQ6" in large block letters, and lists the values of the various run parameters that will actually be used during the run. Some of these parameters appear on the INPUT file. However, the values appearing in the echo written by ECHOZ reflect the adoption of default values and any changes that the code may have made. This echo continues through a listing of "MINERALS LOADED BY INACTIVE BECAUSE OF SUPPRESSION OR LACK OF DATA".

The model in ISWMJP is a redox disequilibrium model (the couple $O_2(aq)/H_2O(l)$ is constrained by a concentration for $O_2(aq)$, while the couple Fe^{3+}/Fe^{2+} is required to satisfy a redox potential of 500 millivolts). EQ6, which currently has no capability to deal with redox disequilibrium, first "equilibrates" the aqueous solution. This requires 12 iterations. The calculated redox potential at this point essentially reflects the presence of the dissolved oxygen, because there is more of it than there is of dissolved iron. The solution is then found to be supersaturated with respect to 33 pure minerals. EQ6 then "equilibrates" the aqueous system by changing the assumed phase assemblage one phase at a time. Dolomite $[CaMg(CO_3)_2]$ is added first. This calculation requires 11 iterations, after which the solution is still supersaturated with respect to only 15 minerals. The common ion effect is responsible for the large reduction in the number of supersaturated phases. Hematite (Fe_2O_3) is added next. This new calculation requires 10 iterations, after which the number of remaining supersaturations is reduced to 10. Addition of muscovite

Figure 8. EQ6 OUTPUT file, OSWEQS.

----- READING THE EQ6 INPUT FILE -----
 INPUT FILE NAME= ISVEGS REVISOR= T.J. VOLERY
 REVISION= 03/16/84

THIS IS A SIMPLE THERMODYNAMIC CALCULATION TO DEMONSTRATE EQ6'S ABILITY TO FIND AN EQUILIBRIUM ASSEMBLAGE OF SOLIDS RESULTING FROM PRECIPITATION FROM A SOLUTION THAT IS SUPERSATURATED WITH RESPECT TO A LARGE NUMBER OF MINERALS. THE FLUID HERE IS SEA WATER, REPRESENTED BY MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON.

THE PHASES PRECIPITATED ARE THOSE THAT ARE THE MOST THERMODYNAMICALLY FAVORED, ACCORDING TO THE THERMODYNAMIC DATA BASE. NO PHASES HAVE BEEN SUPPRESSED, WHICH CAN BE DONE USING THE NXOPT OR NXMOD OPTIONS.

THIS RUN ENDS AFTER THE PRECIPITATION CALCULATIONS ARE COMPLETED. NO IRREVERSIBLE REACTIONS ARE SPECIFIED (NRCT=0). ALSO, THE MAXIMUM NUMBER OF REACTION PROGRESS STEPS IS SET TO ZERO (KSPTMX=0).

```

NMODL= 2
TEMPCE= 2.50000E+01 JTEMP= 0 TK1= 0 TK2= 0 TK3= 0
Z1STRT= 0 Z1MAX= 1.00000E+02
TSTRT= 0 TIMEX= 0
KSTPMX= 0 CPLIM= 0
DZPRNT= 1.00000E+02 DZPRLC= 1.00000E+02 KSPPMX= 0
IFILE= 00
      1 2 3 4 5 6 7 8 9 10
IOPT1-10= 0 0 0 0 0 0 0 0 0 0
I1-20= 0 0
IDPR1-10= 0 0 0 0 0 0 0 0 0 0
IODB1-10= 0 0 0 0 0 0 0 0 0 0
I1-20= 0 0
NXOPT= 0
NRCT= 0
DLZ1OP= 0
TOLB= 0
TOLX= 0
SCREW1= 0
SCREW4= 0
ZKLOGU= 0
DLZMX1= 0
TOLBL= 0
TOLSAT= 0
SCREW2= 0
SCREWS= 0
ZKLOGL= 0
DLZMX2= 0
TOLSST= 0
SCREW3= 0
      0.000
      0.000
INPUT FILE NAME= ISVMJP CREATED= 03/19/84 CREATOR= T.J. VOLERY
SEA WATER TEST CASE, MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM,
  
```

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

AND IRON. THIS IS AN EXTENSION OF THE CLASSIC SEA WATER 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.

THERE IS NO FORCED ELECTRICAL BALANCING IN THIS RUN.

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-
TEMPC1= 2.58888E+01
NXMOD= 1
SPECIES= PD-OXYANIONITE
TYPE= 1
NFFC= 8
KCT= 12
KDIM= 15
OPTION= -1
KMT= 15
KPRS= 8
KLMOD= 8
KKT= 15

COMPONENT      MOLES
O              5.8629223446E+01
NA             4.683778554589E+01
K              1.828768325745569E+02
CA             1.82869261477E+02
MG            5.31495877E+01
AL            7.412348973368611E+08
SI            7.12236E+02
H              1.11E+02
C              2.8995E+05
CL            5.46877648E+02
S              2.8232942E+02
FE            3.581212956E+02
ELECTR        7.93E+02
H2O           1.744365733541414E+08
NA+           -3.466514237287868E+01
K+            -1.998485E+02
CA++          -2.8431929E+02
MG++          -1.334637711162529E+02
AL+++        -1.6978E+02
S1O2(IAC)    -4.174261919974639E+02
H+            -8.125147876E+02
HCO3-         -2.816E+02
CL-           -2.7289214665E+02
SO4--        -1.634119181985116E+02
    
```

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

```
FE++          FE++          -1.346#32643998#88E-#1
OZ(G)         OZ(G)         -1.64299329822#233E-#1
XISTEQ       -2.629#4694#568411E-#1
XI            -1.9327#3489#1918E-#1
```

FILE DATA2 HAS BEEN SUCCESSFULLY READ

FILE DATA3 HAS BEEN SUCCESSFULLY READ

PD-OXYANNITE HAS BEEN USER-SUPPRESSED

```
EEEE 000 666
E   0 0 6
EEEE 0 0 6666
E   0 0 6 6 6
EEEE 000 666
      0
```

EQ6.323FU21
SUPPORTED BY EQL18.323FU22

INPUT FILE NAME= ISWEQS REVISION= 83/16/84 REVISOR= T.J. VOLERY

THIS IS A SIMPLE THERMODYNAMIC CALCULATION TO DEMONSTRATE EQ6'S ABILITY TO FIND AN EQUILIBRIUM ASSEMBLAGE OF SOLIDS RESULTING FROM PRECIPITATION FROM A SOLUTION THAT IS SUPERSATURATED WITH RESPECT TO A LARGE NUMBER OF MINERALS. THE FLUID HERE IS SEA WATER, REPRESENTED BY MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON.

THE PHASES PRECIPITATED ARE THOSE THAT ARE THE MOST THERMODYNAMICALLY FAVORED, ACCORDING TO THE THERMODYNAMIC DATA BASE. NO PHASES HAVE BEEN SUPPRESSED, WHICH CAN BE DONE USING THE NXOPT OR NXMOD OPTIONS.

THIS RUN ENDS AFTER THE PRECIPITATION CALCULATIONS ARE COMPLETED. NO IRREVERSIBLE REACTIONS ARE SPECIFIED (NRCF=0). ALSO, THE MAXIMUM NUMBER OF REACTION PROGRESS STEPS IS SET TO ZERO (KSPTMX=0).

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

INPUT FILE NAME= ISW43P CREATED= 03/19/84 CREATOR= T.J. WOLERY

SEA WATER TEST CASE, MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON. THIS IS AN EXTENSION OF THE CLASSIC SEA WATER 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.

THERE IS NO FORCED ELECTRICAL BALANCING IN THIS RUN.

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.

DATA FILE DATAP.3232U83
1 ATM.-STEAM SATURATION CURVE DATA
LAST REVISED 13 SEPTEMBER 1983 BY D. ISHERWOOD

NO. OF ELEMENTS IN THE DATA BASE = 29
NO. OF ELEMENTS DIMENSIONED FOR = 48
NO. OF ACTIVE ELEMENTS = 12

NO. OF AQUEOUS SPECIES DIMENSIONED FOR = 388
NO. OF AQUEOUS SPECIES LOADED = 95
NO. OF ACTIVE AQUEOUS SPECIES = 52

NO. OF AQUEOUS REACTIONS DIMENSIONED FOR = 289
NO. OF AQUEOUS REACTIONS LOADED = 65
NO. OF ACTIVE AQUEOUS REACTIONS = 48

NO. OF PURE MINERALS DIMENSIONED FOR = 275
NO. OF PURE MINERALS LOADED = 134
NO. OF ACTIVE PURE MINERALS = 127

NO. OF GASES DIMENSIONED FOR = 15
NO. OF GASES LOADED = 7
NO. OF ACTIVE GASES = 7

NO. OF SOLID SOLUTIONS IN THE DATA BASE = 7

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

```

                                NO. OF SOLID SOLUTIONS DIMENSIONED FOR = 28
                                NO. OF ACTIVE SOLID SOLUTIONS = 8

Z1STRT = 8. (INITIAL VALUE OF Z1)
Z1MAX = 1.888888E-08 (MAXIMUM VALUE OF Z1)
TIMEMX = 1.888888E-07 (MAXIMUM VALUE OF TIME, SEC)
KSTPMX = 8 (MAXIMUM NUMBER OF STEPS THIS RUN)

DZPRNT = 1.888888E-08 (LINEAR PRINT INTERVAL)
DZPPLG = 1.888888E-08 (LOGARITHMIC PRINT INTERVAL)
DLZ1DP = 1.888888E-188 (P.R.S. TRANSFER INTERVAL)

MAXIMUM PERMITTED STEP SIZES.....
DLZMK1 = 1.888888E-84 (NORD=8)
DLZMK2 = 1.888888E-07 (NORD.GE.1)

TEMPERATURE = 25.888 C

MHODL1 = 2 (1 = TITRATION, 2 = CLOSED SYSTEM, 3 = FLOW-THROUGH SYSTEM)
MHODL2 = 8 (NOT USED)

IOPT1 = 8 (KINETIC MODE SWITCH)
IOPT2 = 8 (SUPPRESS PHASE BOUNDARY LOCATION)
IOPT3 = 8 (INTERFACING OUTPUT SWITCH)
IOPT4 = 8 (PERMIT SOLID SOLUTIONS SWITCH)
IOPT5 = 8 (REMOVE INITIAL SOLIDS SWITCH)
IOPT6 = 8 (CLEAR P.R.S. AT START SWITCH)
IOPT7 = 8 (NOT CURRENTLY USED)
IOPT8 = 8 (NOT CURRENTLY USED)
IOPT9 = 8 (NOT CURRENTLY USED)
IOPT10 = 8 (BYPASS INITIAL RECALCULATION SWITCH)
IOPT11 = 8 (SUPPRESS ALL REDOX REACTIONS SWITCH)
IOPT12 = 8 (NOT USED)
IFILE = 61 (SUPPLEMENTARY INPUT FILE)

IOPP1 = 8 (PRINT LOADING/NONLOADING OF SPECIES FROM FILES DATA2 AND DATA3)
IOPP2 = 8 (PRINT DERIVATIVES OF BASIS ELEMENTS)
IOPR3 = 8 (PRINT LOADED SPECIES AND LOG K VALUES)
IOPR4 = 8 (PRINT AQUEOUS SPECIES DISTRIBUTION)
IOPR5 = 8 (PRINT CATION/AN- ACTIVITY RATIOS)
IOPR6 = 8 (PRINT ELEMENT/OXIDE COMP. OF MINERAL ASSEMBLAGE)
IOPR7 = 8 (PRINT MINERAL AFFINITY SUMMARY)
IOPR8 = 8 (PRINT GAS FUGACITY SUMMARY)
IOPR9 = 8 (NOT USED)

IODB1 = 8 (ENABLE COMP. MESSAGES)
IODB2 = 8 (ECHO THE DATA FILE READ)
IODB3 = 8 (PRINT ORDER/SCALING INFO.)
IODB4 = 8 (PRINT NEWTON ITERATION INFO.)
IODB5 = 8 (PRINT SEARCH ITERATIONS)
IODB6 = 8 (PRINT HPSATZ ITERATIONS)
IODB7 = 8 (PRINT DERIVATIVES AT EACH PT.)
IODB8 = 8 (TURNS IODB3 AND IODB7 ON AND OFF)
IODB9 = 8 (PRINT KINETICS INFO.)
IODB10 = 8 (CHECK BASIS VAR. F.D. AND T.S.)
IODB11 = 8 (CHECK REAC. RATE F.D. AND T.S.)

```

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

TOLBT = 1.#####E-06 (RESIDUAL FUNCTION CONVERGENCE TOLERANCE)
TOLDL = 1.#####E-06 (CORRECTION TERM CONVERGENCE TOLERANCE)
TOLX = 1.#####E-06 (SEARCH/FIND TOLERANCE)
TOLSAT = 8.#####E-05 (LOWER SUPERSATURATION TOLERANCE)
TOLSST = 1.#####E-04 (UPPER SUPERSATURATION TOLERANCE)

SCREW1 = 1.####E-05 (STEP-SIZE CONTROL PARAMETER FOR BASIS VARIABLES)
SCREW2 = .#####E (AUXILIARY STEP SIZE PARAMETER FOR BASIS VARIABLES)
SCREW3 = 1.####E-05 (STEP SIZE CONTROL PARAMETER FOR RATE FUNCTIONS)
SCREW4 = 1.####E-04 (CORRECTOR CONTROL PARAMETER FOR RATE FUNCTIONS)
SCREW5 = 2.####E (UNDER-RELAXATION CONTROL FOR NEWTON RAPHSON ITERATION)

ZKLOGU = -8.### (THRESHOLD LOG MASS FOR SOLIDS)
ZKLOGL = 1.### (LOG MASS DECREMENT FOR P.R.S SHIFT)

IACON = 16. CL- (DEFINES XISTEQ)

AQUEOUS SPECIES LOADED BUT INACTIVE BECAUSE OF SUPPRESSION OR LACK OF DATA

SR**
ZN**
PB**
AG**
BA**
NH4**
F-
HG**
AS(OH)4-
NH**
CU*
AU*
U***
HPO4--
VO**
PUD2**
CS*
N2(AQ)
CN(AQ)
U***
HG2**
AS(OH)6---
NH**
CU**
AU***
UG2**
UC2**
PUD2*
PU***
NO3-
H2PO4-
ClO4-
FCL
KCO3-
FECL*
FECL2

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

FECL3-
 FECL4--
 FE(SO4)2-
 KOH
 MGCL•

MINERALS LOADED BUT INACTIVE BECAUSE OF SUPPRESSION OR LACK OF DATA

ANTIGORITE
 7A-BAPHNITE
 PD-OXYANNITE
 LEONHARDITE
 CO2(G)
 O2(G)
 NA2SO4

 STEPPING TO...(NORD = #)... ZI = #. . DELZI = #. . TIME = #. . D. DTIME = #. .

ATTEMPTED SPECIES ASSEMBLAGE NO. 1

1	1	O
2	2	NA
3	3	K
4	4	CA
5	8	MG
6	6	AL
7	7	SI
8	13	H
9	14	C
10	16	CL
11	17	S
12	22	FE
13		CHARGE BALANCE
14		H2TEO
15		HI

ITER = 12
 33 SUPERSATURATED PURE MINERALS
 8 SUPERSATURATED SOLID SOLUTIONS

THE MOST SUPERSATURATED PHASES		AFFINITY, KCAL	
1	17	DOLOMITE	4.65278131
2	95	ORDERED DOLOMITE	4.65278131
3	18	MAGNESITE	1.34947668
4	95	DISORDERED DOLOM	2.54294269
5	14	CALCITE	1.87859327
6	33	TALC	7.84832543
7	62	ARAGONITE	.85348622
8	48	MUNTITE	2.76271669

ATTEMPTED SPECIES ASSEMBLAGE NO. 2

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

```

1 1 O
2 2 NA
3 3 K
4 4 CA
5 5 MG
6 6 AL
7 7 SI
8 13 H
9 14 C
10 16 CL
11 17 S
12 22 FE
13 CHARGE BALANCE
14 XISTEG
15 XI
16 17 DOLOMITE

```

ITER = 11
15 SUPERSATURATED PURE MINERALS
8 SUPERSATURATED SOLID SOLUTIONS

THE MOST SUPERSATURATED PHASES			AFFINITY, KCAL
1	8	HEMATITE	22.78214235
2	92	MG-NONTRONITE	24.81465928
3	93	NA-NONTRONITE	24.82215194
4	91	CA-NONTRONITE	23.87482228
5	94	K-NONTRONITE	23.78185891
6	93	H-NONTRONITE	22.72777688
7	6	MAGNETITE	9.64599179
8	93	ANDRADITE	4.71624539

ATTEMPTED SPECIES ASSEMBLAGE NO. 3

```

1 1 O
2 2 NA
3 3 K
4 4 CA
5 5 MG
6 6 AL
7 7 SI
8 13 H
9 14 C
10 16 CL
11 17 S
12 22 FE
13 CHARGE BALANCE
14 XISTEG
15 XI
16 8 HEMATITE
17 17 DOLOMITE

```

ITER = 14
12 SUPERSATURATED PURE MINERALS
8 SUPERSATURATED SOLID SOLUTIONS

THE MOST SUPERSATURATED PHASES			AFFINITY, KCAL
1	35	MUSCOVITE	2.87854829

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

2	83	NA-NONTRONITE	1.38321959
3	92	MG-NONTRONITE	1.32961667
4	91	CA-NONTRONITE	1.89888873
5	84	K-NONTRONITE	1.87641656
6	38	KAOLINITE	.74574986
7	11	GIBBSITE	.23436813
8	53	K-FELDSPAR	.12469928

ATTEMPTED SPECIES ASSEMBLAGE NO. 4

1	1	O
2	2	NA
3	3	K
4	4	CA
5	5	MG
6	6	AL
7	7	SI
8	13	H
9	14	C
10	16	CL
11	17	S
12	22	FE
13		CHARGE BALANCE
14		MISTEG
15		XI
16	8	NEMATITE
17	17	SOLOPITE
18	35	MUSCOVITE

ITER = 6
 4 SUPERSATURATED PURE MINERALS
 8 SUPERSATURATED SOLID SOLUTIONS

THE MOST SUPERSATURATED PHASES			AFFINITY, KCAL
1	83	NA-NONTRONITE	1.29782548
2	92	MG-NONTRONITE	1.82432284
3	91	CA-NONTRONITE	.81366581
4	84	K-NONTRONITE	.79122289

ATTEMPTED SPECIES ASSEMBLAGE NO. 5

1	1	O
2	2	NA
3	3	K
4	4	CA
5	5	MG
6	6	AL
7	7	SI
8	13	H
9	14	C
10	16	CL
11	17	S
12	22	FE
13		CHARGE BALANCE
14		MISTEG
15		XI
16	8	NEMATITE

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

17 17 DOLOMITE
 18 35 MUSCOVITE
 19 83 NA-MONTRONITE

----- ITERATION HAS GONE SOUR (ITER = 14) -----
 THE PHASE TO BE DROPPED IS HEMATITE

(8)

ATTEMPTED SPECIES ASSEMBLAGE NO. 6

1 1 O
 2 2 NA
 3 3 K
 4 4 CA
 5 5 MC
 6 6 AL
 7 7 SI
 8 13 H
 9 14 C
 10 16 CL
 11 17 S
 12 22 FE
 13 CHARGE BALANCE
 14 MIXTEQ
 15 NI
 16 17 DOLOMITE
 17 35 MUSCOVITE
 18 83 NA-MONTRONITE

ITER = 6

 REACTION PROGRESS = 0.
 LOG OF REACTION PROGRESS = -555.000000
 TEMPERATURE = 25.000 DEGREES C
 TOTAL PRESSURE = 1.013 BARS
 COMPUTING UNITS REMAINING = 0.000

CHANGE OR ATTEMPTED CHANGE IN THE PHASE ASSEMBLAGE
 START OR RE-START OF RUN
 MAXIMUM NUMBER OF STEPS

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	8.898874E+05	8.862788E+01	8.862788E+01
NA	1.8482348E+04	4.683774E-01	4.683778E-01
K	3.855957E+02	1.228766E-02	1.228767E-02
CA	3.884895E+02	1.873237E-02	1.873238E-02

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

MG	1.242184E-03	6.289499E-02	6.289501E-02
AL	4.637878E-04	1.748447E-06	1.748448E-06
SI	1.929763E-08	7.111786E-05	7.111788E-05
M	1.881186E-05	1.118285E-02	1.118285E-02
C	1.845938E-01	1.598788E-03	1.598788E-03
CL	1.845938E-04	5.458776E-01	5.458776E-01
S	8.746154E-02	2.823293E-02	2.823294E-02
FE	3.656718E-12	6.777896E-17	6.777898E-17
CO3--		1.598788E-03	1.598788E-03
SO4--		2.823293E-02	2.823294E-02
S--		6.475371-141	6.475373-141

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

OXYGEN FUGACITY = 1.85922E-01
 LOG OXYGEN FUGACITY = -.72839
 EM = .82337 VOLTS
 PE = 13.91849

PH = 6.57925
 ACTIVITY OF WATER = .98283
 LOG ACTIVITY OF WATER = -.01717
 ALKALINITY = 1.323828E-03 EQUIV/KG SOLVENT (NOT DEF. FOR T.C.T.55 C)

IONIC STRENGTH = 6.399794E-01 MOLAL
 EQUIV. STOICH. IONIC STRENGTH = 5.458776E-01 MOLAL

MASS OF SOLUTION = 1.835528 KG
 MASS OF SOLVENT = 1.835528 KG
 MASS OF SOLUTES = .035528 KG
 CONC OF SOLUTES = 3.386245 PER CENT (W/W)

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG C	LOG ACT
H2O	5.55893E-01	1.00000E-03				
NA+	4.63787E-01	1.073492E-01	4.58163E-01	-.34663	-.17242	-.51925
K+	1.88118E-02	3.92364E-01	1.88354E-02	-1.99847	-.28168	-2.28886
CA++	8.86795E-03	3.55428E-01	8.86795E-03	-2.05218	-.68634	-2.68852
MG++	4.62251E-02	1.12358E-08	4.62258E-02	-1.33512	-.49919	-1.83432
AL+++	3.67221E-12	9.63854E-11	3.67221E-12	-11.44786	-1.86368	-12.51274
SI(O2(AO))	7.89863E-05	4.26514E-03	7.89863E-05	-4.14883	8.88882	-4.14883
M+	2.68582E-07	2.62586E-07	2.68582E-07	-6.58419	-.89486	-6.67985
CO3--	6.63632E-07	5.18257E-05	6.63632E-07	-6.86367	-.72856	-6.78423
CL-	5.33465E-01	1.09129E-01	5.33464E-01	-.27289	-.28168	-.47449
SO4--	1.46629E-02	1.48849E-08	1.46629E-02	-1.83378	-.76839	-2.68217
FE++	1.29826E-23	7.28582E-22	1.29826E-23	-22.88932	-.68634	-23.49566
O2(AO)	2.81548E-04	6.44934E-03	2.81548E-04	-3.69562	8.6823	-3.62739
H2(AO)	4.21389E-45	8.49521E-45	4.21389E-45	-44.37532	8.6823	-44.38788
HS-	6.47537-141	2.14128-139	6.47537-141	-148.18874	-.18681	-148.37475
FE+++	2.98957E-22	1.66959E-28	2.98957E-22	-21.52439	-1.86368	-22.58887
HCO3-	1.83593E-03	6.46738E-02	1.83593E-03	-2.97472	-.18646	-3.13518
OH-	7.48945E-08	1.26813E-06	7.48945E-08	-7.13821	-.18681	-7.13822
AL(OH)++	1.18111E-18	4.84369E-09	1.18111E-18	-9.95817	-.68634	-18.56451
AL(OH)14-	1.72896E-08	1.64278E-06	1.72896E-08	-7.76222	-.17242	-7.93463
PSO4-	1.72266E-04	2.32828E-02	1.72266E-04	-3.76382	-.18681	-3.94981

Figure 8. EQ6 OUTPUT file, OSWEQS (Continued).

NaCl	1.24138E-02	7.25454E-01	1.24138E-02	-1.98612	0.00000	-1.98612
NaCO3-	6.56942E-07	5.45256E-05	6.56942E-07	-6.18247	-0.16246	-6.34293
NaSO4-	5.82184E-03	6.92597E-01	5.82184E-03	-2.23649	-0.16587	-2.40236
CaCO3	5.69533E-07	5.72248E-05	5.69533E-07	-6.24448	0.00000	-6.24448
CaMCO3+	4.82262E-05	4.54653E-03	4.82262E-05	-4.39766	-0.14555	-4.54321
CaSO4	1.12382E-03	1.52995E-01	1.12382E-03	-2.94938	0.00000	-2.94938
MgCO3	2.38495E-06	1.94348E-04	2.38495E-06	-6.53734	0.00000	-6.53734
MgMCO3+	1.94629E-04	1.66861E-02	1.94629E-04	-3.71879	-0.17242	-3.89121
MgSO4	6.47284E-03	7.79292E-01	6.47284E-03	-2.18891	0.00000	-2.18891
MgSiO4-	1.38787E-07	1.24359E-05	1.38787E-07	-6.85354	-0.17242	-7.02596
HSO4-	7.87496E-08	7.64399E-06	7.87496E-08	-7.18375	-0.17242	-7.35617
MgCO3	2.91728E-04	1.82939E-02	2.91728E-04	-3.63553	0.56823	-3.06730
Mg(OH) ⁺	1.71787E-07	7.89687E-06	1.71787E-07	-6.76581	-0.17242	-6.93823
Ca(OH) ⁺	3.95588E-09	2.25784E-07	3.95588E-09	-6.48284	-0.17242	-6.65526
NaOH	2.91561E-09	1.16615E-07	2.91561E-09	-8.53527	0.00000	-8.53527

----- SUMMARY OF SOLID PRODUCT PHASES-----

PRODUCT	LOG MOLES	MOLES	GRAMS	VOLUME, CC
DOLOMITE	-3.5942266	2.54557E-04	4.69398E-02	1.63778E-02
MUSCOVITE	-7.7711727	1.69367E-08	6.74621E-06	2.38316E-06
NA-NONTRONITE	-7.7469998	1.79861E-08	7.61486E-06	2.36539E-06

	MASS, GRAMS	VOLUME, CC
CREATED	4.695418E-02	1.638251E-02
DESTROYED	0.	0.
NET	4.695418E-02	1.638251E-02

WARNING-- THESE VOLUME TOTALS MAY BE INCOMPLETE

----- MINERAL SATURATION STATE SUMMARY -----

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
PHENGITE	-1.4385		CORUNDUM	-8.6695	
HEMATITE	-1.2961		DEHYDRATED ANALC	-9.8247	
BRUCITE	-6.7278		GIBBSITE	-6.6242	
MALITE	-3.8586		SILVITE	-4.8699	
CALCITE	-1.2522		MAGNESITE	-9.9698	
DOLOMITE	0.0000	SATD	ANHYDRITE	-1.3579	
GYPNUM	-0.5818		QUARTZ	-2.2848	
MAXIMUM MICROCL	-0.7367		LOW ALBITE	-2.5555	
NEPHELINE	-6.2916		ANALCIME	-2.6124	
KADOLINITE	-0.9733		CHRYSOTILE	-7.2584	
PYROPHYLITE	-3.5934		TALC	-4.9363	
NA-BEIDELLITE	-2.8252		MUSCOVITE	0.0000	SATD
ILLITE	-2.8257		ARTINITE	-9.1768	
ENSTATITE	-5.5959		DIOPSIDE	-9.6312	
WOULASTONITE	-9.6684		KYANITE	-7.3876	
MURTITE	-6.5259		AMORPHOUS SILICA	-1.9881	
PHLOGOPITE	-5.6481		K-FELDSPAR	-0.7367	
HIGH SANIDINE	-2.3728		HIGH ALBITE	-4.3545	
K-BEIDELLITE	-3.1318		CA-BEIDELLITE	-3.1894	

[$KAl_3Si_3O_{10}(OH)_2$] requires 6 iterations, and only 4 supersaturations then remain.

Addition of Na-nontronite [$Na_{0.33}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2$] gives a different result. The iteration diverges, stopping after 14 iterations. This happens because hematite and Na-nontronite can not both be in the equilibrium phase assemblage. EQ6's phase deletion algorithm (Section 7.6) examines the wreckage, and concludes that hematite should be deleted. The calculation that follows then requires 6 iterations, and no supersaturations remain.

The remainder of the OUTPUT file consists of a detailed description of the state of the system, written by subroutine SCRIPZ. Such a printout is not made at every step of reaction progress, but only at so-called "print points." In this case, reaction progress begins and ends at zero, so there is only one such printout. Note that it gives the composition of the aqueous solution, including pH and redox potential (which are outputs of the calculation, not fixed inputs as in some other geochemical codes that make precipitation calculations). This includes the detailed speciation of the solution. Also given are the masses of product minerals precipitated, and a summary of the mineral saturation relations.

6.2.2. CALCULATING HIGH TEMPERATURE PH FROM QUENCH PH

This example illustrates EQ6's capability to calculate high temperature properties from measurements on fluid samples that have been quenched (cooled to room temperature). The problem here is to calculate the at-temperature pH of the fluid in an autoclave experiment from a measurement of quench pH. This calculation also yields other at-temperature properties, such as redox potential and mineral saturation indices.

To make such a calculation, EQ3NR must first be used to calculate a model of the quenched fluid. The EQ3NR INPUT file used in this example, IDB201, is presented in Figure 9. Note that the analysis of the fluid must be essentially complete. The PICKUP file from this run was used as the lower part of the EQ6 INPUT file, IHDB201, shown in Figure 10.

This EQ6 run illustrates a temperature jump. The temperature of the quenched fluid sample was assumed to be 25°C, while the temperature of the experiment was 250°C. Although it is possible to calculate the state of the system at intermediate temperatures by specifying a reaction progress run in which temperature increases with reaction progress, there is no point in doing so in this case. Thus, the initial temperature in the EQ6 run is the desired final temperature. This problem required 3.33 seconds (CPU = 2.35 seconds) on a CDC 7600 computer.

The last four pages of the OUTPUT file for this example are shown in Figure 11. This calculation took 7 iterations to complete. The calculation gives the 250°C pH as 7.21, up from 6.44 at 25°C. The solution was calculated to be multiply-supersaturated, which is a realistic result, considering that the fluid was sampled after only one day of reaction at 250°C with ground tuff. No minerals were precipitated in this EQ6 run because precipitation was globally suppressed by means of the subset-selection suppression option "ALL".

Figure 9. EQ3NR INPUT file, IDB201.

INPUT FILE NAME= IDB201 REVISED 03/19/84 REVISOR= T.J. WOLERY

ANALYSIS OF WATER TAKEN AT 1 DAY FROM EXPERIMENT DB2. IN WHICH CRUSHED TOPOPAH SPRINGS TUFF (TPT) AND WELL J-13 WATER WERE REACTED IN A DICKSON AUTOCLAVE AT 250 DEG C AT IN INITIAL ROCK/WATER RATIO OF 42.16 G/KG (7.5456G/176.9ML). THESE RESULTS WERE REPORTED BY K. KNAUSS (9/30/83).

EXPERIMENTAL NOTES-

1. THE TUFF IS AN OUTCROP SAMPLE FROM FRAN RIDGE.
2. IT WAS PRETREATED BY COOKING IN DEIONIZED WATER AT 150 C FOR ONE DAY TO REMOVE SOLUBLE SALTS (BATCH A2).
3. EXPERIMENT WAS TO RUN FOR 60 DAYS. FAILED AT 47 DAYS.
4. SI DATA WERE OBTAINED FROM 10X DILUTED SAMPLE.
5. THE MEASURED PH IS THE QUENCH PH AT 25 DEG C.

TEMPC=	25.										
RHO=	1.0										
FEP=	-0.68										
TOLET=	0.										
ITERMX=	0										
IOP1-10=	0	0	0	0	0	0	0	0	0	0	0
IPRNT1-10=	0	0	0	0	0	0	0	0	0	0	0
IDBUG1-10=	0	0	0	0	0	0	0	0	0	0	0
UEBAL=											
NXMOD=	1										
SPECIES=	PD-OXYANKITE										
TYPE=	1										
		NA+									
		K+									
		CA++									
		MG++									
		AL+++									
		SiO2(AQ)									
		H+									
		HCO3-									
		NO3-									
		CL-									
		SO4--									
		F-									
		FE++									
		MN++									
		O2(AQ)									
		H2(AQ)									
		N2(AQ)									
		NH4+									
		CO3--									
NO3-											
HCO3-											
ENDIT.											

Figure 10. EQ6 INPUT file, IHDB201.

INPUT FILE NAME= IHDB201 REVISED 03/19/84 REVISOR= T.J. WOLERY

THIS RUN CALCULATES THE IN SITU PROPERTIES OF THE AUTOCLAVE WATER SAMPLE DESCRIBED BELOW IN THE EQ3NR TITLE. THESE IN SITU PROPERTIES INCLUDE THE AT-TEMPERATURE PH AND MINERAL SATURATION INDICES. THIS CALCULATION IS AN EXAMPLE OF A TEMPERATURE JUMP, IN THIS CASE FROM 25 DEG C TO 250 DEG C.

NO MINERALS ARE PERMITTED TO PRECIPITATE. THIS IS SPECIFIED BY THE SUBSET-SELECTION SUPPRESSION OPTION GIVEN BELOW ('NXOPT= 1' FOLLOWED BY 'OPTION= ALL').

```

-----
NMODL1= 2
TEMPCE= 250. JTEMP= 0
TK1= 0. TK2= 0. TK3= 0.
ZISTR1= 0. ZIMAX= 1.
TSTR1= 0. TIMEMX= 1.E+0
KSTPMX= 0. CPLIM= 0.
DZ1PR= 1.E+5 DZPRLG= 0.5
IFILE= 60
IOPT1-10= 0 0 0 0 0 0 0 0 0 0
11-20= 0 0
IOPR1-10= 0 0 0 0 0 0 0 0 1 0 0
IOBE1-10= 0 0 0 0 0 0 0 0 0 0 0
11-20= 0 0
NXOPT= 1
OPTION= ALL
HXOPEX= 0
NRCT= 0
-----
DLZ1DP= 0. TOLDL= 0. TOLX= 0.
TOLBT= 0. TOLSST= 0.
TOLSAT= 0. TOLSS2= 0. SCREW3= 0.
SCREW1= 0. SCREW2= 0.
SCREW4= 0. SCREW5= 0.
ZKLOGU= 0. ZKLOGL= 0.
DLZMX1= 0. DLZMX2= 0.
-----
* PICKUP FILE WRITTEN BY EQ3NR.3230U52
* SUPPORTED BY EQLB.3230U02
INPUT FILE NAME= IHDB201 REVISED 03/19/84 REVISOR= T.J. WOLERY

```

Figure 10. EQ6 INPUT file, IHDB201 (Continued).

ANALYSIS OF WATER TAKEN AT 1 DAY FROM EXPERIMENT DB2. IN WHICH CRUSHED TOPOPAH SPRINGS TUFF (TPT) AND WELL J-13 WATER WERE REACTED IN A DICKSON AUTOCLAVE AT 250 DEG C AT IN INITIAL ROCK/WATER RATIO OF 42.18 G/KG (7.5456G/178.9ML). THESE RESULTS WERE REPORTED BY K. KNAUSS (9/30/83).

EXPERIMENTAL NOTES-

1. THE TUFF IS AN OUTCROP SAMPLE FROM FRAN RIDGE.
2. IT WAS PRETREATED BY COOKING IN DEIONIZED WATER AT 150 C FOR ONE DAY TO REMOVE SOLUBLE SALTS (BATCH A2).
3. EXPERIMENT WAS TO RUN FOR 60 DAYS, FAILED AT 47 DAYS.
4. SI DATA WERE OBTAINED FROM 10X DILUTED SAMPLE.
5. THE MEASURED PH IS THE QUENCH PH AT 25 DEG C.

```

UACION= NA+
TEMPCI= 2.50000E+01
NXMOD= 1
SPECIES= PD-OXYANNITE
TYPE= 1
NFFG= 0
KCT= 15
KDJM= 10
OPTION= -1
KMT= 10
KPRS= 0
XLKMOD= 0.
KXT= 10

O 5.554251611156201E+01
NA 2.105263157094721E-03
K 3.094707457150903E-04
CA 3.443113772455173E-05
MG 1.308372762005905E-05
AL 2.864872670215151E-04
SI 1.121762065321074E-02
H 1.110232994595590E+02
C 2.647239065520460E-03
N 1.774050479000013E-04
CL 2.341127690101476E-04
S 2.196569500473907E-04
F 1.4738393515100695E-04
MN 7.644981615639457E-07
FE 5.156946657033153E-06
ELECTR -9.8271360063535700E-06
H2O H2O 1.744365733541414E+00
NA+ NA+ -2.077095453243652E+00
K+ K+ -3.509097361390031E+00
CA++ CA++ -4.484075243486003E+00
MG++ MG++ -4.900294106234199E+00
AL+++ AL+++ -7.126216017027929E+00
SIO2(AQ) SIO2(AQ) -1.950439706002314E+00

```

Figure 10. EQ6 INPUT file, IHDB201 (Continued).

H+	H+	-6.416595678231459E+88
HCO3-	CO3--	-2.823458331218481E+88
NO3-	NH4+	-3.751834826676393E+88
CL-	CL-	-3.638674281968688E+88
SO4--	SO4--	-3.665249264771361E+88
F-	F-	-4.774532125448516E+88
MN++	MN++	-6.298837343243829E+88
FE++	FE++	-1.212742886563738E+81
O2(G)	O2(G)	-6.799999999999997E-81
XISTEQ		-2.676693689624849E+88
XI		-2.543378132527896E+88

Figure 11. The EQ6 OUTPUT file, OHDB201 (Last four pages only).

ATTEMPTED SPECIES ASSEMBLAGE NO. 1

```

1 1 O
2 2 NA
3 3 K
4 4 CA
5 5 MG
6 6 AL
7 7 SI
8 13 H
9 14 C
10 15 N
11 16 CL
12 17 S
13 18 F
14 21 MH
15 22 FE
16 CHARGE BALANCE
17 MIXTED
18 XI
    
```

ITER = 7

```

REACTION PROGRESS = 0.
LOG OF REACTION PROGRESS = -689.8888888
TEMPERATURE = 258.888 DEGREES C
TOTAL PRESSURE = 39.776 BARS
COMPUTING UNITS REMAINING = 8.888
    
```

START OR RE-START OF RUN
 MAXIMUM NUMBER OF STEPS

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	8.877823E-05	8.854298E-01	8.854298E-01
NA	4.835242E-01	2.185281E-03	2.185263E-03
K	1.228832E-01	3.2294814E-04	3.2294787E-04
CA	1.378657E-02	3.447143E-05	3.443114E-05
MG	3.176986E-01	1.388384E-05	1.388373E-05
AL	7.722347E-02	2.864837E-04	2.864873E-04
SI	3.147462E-02	1.121772E-02	1.121763E-02
H	1.117918E-01	1.118242E-02	1.118233E-02
C	3.176575E-01	2.647261E-03	2.647239E-03
N	2.462442E-02	1.774865E-04	1.774858E-04
CL	8.291924E-02	2.341147E-04	2.341128E-04
S	7.235414E-02	2.196688E-04	2.196692E-04
F	2.757325E-02	1.473852E-04	1.473839E-04

Figure 11. The EQ6 OUTPUT file, OHDB201 (Continued).

MN	4.195913E-02	7.648546E-07	7.644992E-07
FE	2.877198E-01	6.156992E-06	6.156947E-06
CO3--		2.647261E-03	2.647239E-03
SO4--		2.196678E-04	2.196592E-04
S--		6.686665E-74	6.686628E-74

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

OXYGEN FUGACITY = 1.25518E-01
 LOG OXYGEN FUGACITY = -.91896
 EM = .44836 VOLTS
 PE = 4.24438

PH = 7.28762
 ACTIVITY OF WATER = .99993
 LOG ACTIVITY OF WATER = -.00003
 ALKALINITY = #. EQUIV/KG SOLVENT (NOT DEF. FOR T.CT.SB C)

IONIC STRENGTH = 2.618543E-03 MOLAL
 EQUIV. STOICH. IONIC STRENGTH = 2.185281E-03 MOLAL

MASS OF SOLUTION = 1.882974 KG
 MASS OF SOLVENT = .999992 KG
 MASS OF SOLUTES = .882982 KG
 CONC OF SOLUTES = .882143 PER CENT (W/W)

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG G	LOG ACT
H2O	6.55788E-01	9.99992E-02				
NA+	2.89185E-03	4.82848E-02	2.89157E-03	-2.67953	-.84635	-2.72688
K+	2.88543E-04	1.16724E-02	2.98545E-04	-3.52499	-.84722	-3.57219
CA++	2.48878E-06	3.79958E-04	9.48880E-06	-5.82319	-.17922	-5.28241
MG++	4.93912E-07	1.28245E-05	4.93915E-07	-6.30536	-.17322	-6.47954
AL+++	4.89786E-28	1.12568E-18	4.89789E-28	-19.38744	-.38337	-19.77281
STO2(AG)	1.11923E-02	6.72481E-01	1.11924E-02	-1.95188	.88882	-1.95188
H+	6.83748E-08	6.89212E-08	6.83746E-08	-7.16511	-.84252	-7.28762
CO3--	4.74448E-08	2.84727E-06	4.74444E-08	-7.32382	-.18482	-7.88783
SO4--	4.36848E-36	7.87445E-35	4.36851E-36	-35.35996	-.84764	-35.48768
CL-	2.33654E-04	8.28374E-03	2.33656E-04	-3.63142	-.84728	-3.67863
F-	1.73381E-04	1.68946E-02	1.73382E-04	-3.76188	-.18567	-3.94667
MN++	1.31286E-04	2.49418E-03	1.31287E-04	-3.88178	-.84677	-3.92855
FE++	6.98777E-06	3.83894E-06	6.98783E-06	-7.15566	-.17922	-7.33488
O2(AG)	7.98638E-28	4.46215E-18	7.98644E-28	-19.89765	-.17922	-19.27686
H2(AG)	2.63437E-04	8.42974E-03	2.63448E-04	-3.57932	.88236	-3.57896
HS-	3.15891E-23	6.35223E-23	3.15894E-23	-22.52156	.88236	-22.52122
FE+++	6.68666E-74	2.21195E-72	6.68656E-74	-73.17488	-.84637	-73.22157
NO3-	1.22223E-26	6.82579E-25	1.22224E-26	-25.91284	-.38337	-25.29621
NH4+	1.77485E-04	1.18888E-02	1.77487E-04	-3.75183	-.84722	-3.79823
NH3	1.75894E-03	6.46136E-02	1.75895E-03	-2.97512	-.84594	-3.82186
OH-	1.46643E-04	2.49295E-03	1.46644E-04	-3.83374	-.84677	-3.88251
AL(OH)++	4.83776E-11	1.99611E-09	4.83782E-11	-12.34315	-.17922	-12.82237
AL(OH)A-	2.86392E-04	2.72184E-02	2.86394E-04	-3.84384	-.84635	-3.88939
KCL	2.81386E-06	2.89716E-06	2.81388E-06	-7.55882	.88882	-7.55882
K2SO4	1.89861E-05	1.47432E-03	1.89862E-05	-4.96225	-.84677	-5.88282
NaCl	4.32439E-07	2.61561E-05	4.32443E-07	-6.36688	.88882	-6.36688

Figure 11. The EQ6 OUTPUT file, OHDB201 (Continued).

NAC03-	1.84791E-#8	1.28478E-#6	1.84792E-#8	-7.81828	-.84594	-7.85619
NAS04-	1.22513E-#5	1.45848E-#3	1.22514E-#5	-4.91181	-.84618	-4.95792
CAC03	2.73239E-#7	2.73482E-#5	2.73242E-#7	-6.56346	0.00000	-6.56346
CANCO3-	4.18530E-#6	4.28888E-#4	4.18534E-#6	-5.38139	-.84637	-5.42676
CAS04	1.48765E-#5	2.82525E-#3	1.48766E-#5	-4.82758	0.00000	-4.82758
MCC03	8.31316E-#9	4.47974E-#7	8.31328E-#9	-8.27464	0.00000	-8.27464
MCMCO3-	9.22846E-#8	7.86725E-#6	9.22873E-#8	-7.23523	-.84635	-7.28159
MCS04	8.82588E-#6	7.81228E-#4	8.82593E-#6	-6.23463	0.00000	-6.23463
MNS04	3.82815E-#7	4.86832E-#5	3.82818E-#7	-6.51997	0.00000	-6.51997
MNS104-	2.82832E-#5	2.88461E-#3	2.82834E-#5	-4.69716	-.84635	-4.64362
MSO4-	2.11452E-#6	2.85248E-#4	2.11454E-#6	-6.67478	-.84635	-6.72114
MZCO3	1.88363E-#3	9.82249E-#2	1.88365E-#3	-2.88834	0.00000	-2.79998
MG10H)-	8.73391E-#6	2.36879E-#4	8.73395E-#6	-5.24185	-.84635	-5.28758
CA10H)-	2.36827E-#6	1.35197E-#4	2.36829E-#6	-5.62557	-.84635	-5.67152
FE10H)4-	8.18695E-#5	6.28822E-#4	8.18699E-#5	-5.28768	-.84635	-5.33396
NAOH	2.88482E-#7	1.83352E-#5	2.88482E-#7	-6.88778	0.00000	-6.88778
MN10H)-	2.78734E-#7	1.98593E-#5	2.78736E-#7	-6.55983	-.84635	-6.60539
MNCO3	7.25437E-#8	8.33868E-#6	7.25443E-#8	-4.96927	0.00000	-7.13948
HF	1.87331E-#6	2.14726E-#4	1.87332E-#6	-7.96927	0.00000	-4.96927
HF2-	1.96845E-#8	7.67795E-#7	1.96847E-#8	-7.28587	-.84635	-7.75222
NAF	7.82788E-#7	3.16877E-#5	7.82788E-#7	-6.12333	0.00000	-6.12333
MGF+	9.32518E-#7	4.83885E-#5	9.32518E-#7	-6.83834	-.84635	-6.87659
CAF+	3.27787E-#6	1.93658E-#4	3.27798E-#6	-5.48448	-.84635	-5.53876
MNF+	4.48272E-#8	3.25528E-#6	4.48276E-#8	-7.35627	-.84635	-7.48253
ALF2+	1.43496E-#9	9.32429E-#8	1.43497E-#9	-8.84316	-.84635	-8.88951
ALF3	6.89872E-#8	5.12152E-#6	6.89877E-#8	-7.21476	0.00000	-7.21476
ALF4-	3.27748E-#8	3.27499E-#6	3.27751E-#8	-7.48446	-.84635	-7.53881
ALF5--	2.16228E-1E	2.63741E-#8	2.16229E-1E	-8.56589	-.18567	-9.85876

MASS, GRAMS VOLUME, CC
 CREATED #. #.
 DESTROYED #. #.
 NET #. #.
 WARNING-- THESE VOLUME TOTALS MAY BE INCOMPLETE

----- MINERAL SATURATION STATE SUMMARY -----

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
ANTIGORITE	214.9582	SSATD	PHENGITE	9.8736	SSATD
MAGNETITE	-6.3847		CORUNDUM	2.6927	SSATD
HEMATITE	9.4628	SSATD	DEHYDRATED ANALC	-1.8678	
BRUCITE	-1.2686		SIBSITITE	.9448	SSATD
REYAJANES SMECTI	17.8546	SSATD	CALCITE	1.4795	SSATD
MACHESITE	.4418	SSATD	RHODOCHROSITE	.6813	SSATD
DOLOMITE	2.9682	SSATD	ANHYDRITE	-1.7877	
GYPSPUM	-5.9247		QUARTZ	.8628	SSATD
MAXIMUM MICROCLT	8.6885	SSATD	LOW ALBITE	4.8182	SSATD
ANOPHTHITE	9.7868	SSATD	SEPIOLITE	8.8743	SSATD
14A-AMESITE	34.2877	SSATD	NEPHELINE	-.3825	
GEMLENITE	-2.9718		ANALCIME	3.8866	SSATD
KAD. INITE	7.8947	SSATD	CHRYSOTILE	12.2671	SSATD
PYROPHYLLITE	7.8327	SSATD	TALC	17.9117	SSATD
NA-BEIDELLITE	9.8236	SSATD	MUSCOVITE	14.6457	SSATD
ILLITE	11.3763	SSATD	TREMOLITE	35.6679	SSATD

Figure 11. The EQ6 OUTPUT file, OHDB201 (Continued).

ENSTATITE	2.8829	SSATD	DIOPSIDE	7.8811	SSATD
MOLLASTONITE	-0.6183		ZOISITE	17.5922	SSATD
KYANITE	4.2825	SSATD	FORSTERITE	3.6445	SSATD
PREHNITE	14.2781	SSATD	MUMITE	.9631	SSATD
AMORPHOUS SILICA	-0.6458		14A-RIPIDOLITE	-9.4234	
PHLOGOPITE	28.6863	SSATD	ANHYDROUS CORDIE	18.1471	SSATD
K-FELDSPAR	6.4733	SSATD	HIGH SANIDINE	4.6371	SSATD
HIGH ALBITE	3.6437	SSATD	HYDROUS CORDIERI	17.4827	SSATD
K-BEIDELLITE	9.2582	SSATD	CA-BEIDELLITE	11.4774	SSATD
MG-BEIDELLITE	11.8723	SSATD	M-BEIDELLITE	9.2348	SSATD
ARAGONITE	1.8714	SSATD	NA-SAPONITE	19.7238	SSATD
K-SAPONITE	19.1683	SSATD	CLINOZOISITE	17.6385	SSATD
MANGANOSITE	-4.4417		PARAGONITE	12.3535	SSATD
SPINEL	3.8886	SSATD	DIASPORE	2.3598	SSATD
CA-SAPONITE	21.3797	SSATD	BOENMITE	1.9151	SSATD
CHALCEDONY	.2122	SSATD	MG-SAPONITE	21.4397	SSATD
7A-CLINOCHLORE	26.5737	SSATD	ANDALUSITE	4.4831	SSATD
M-SAPONITE	18.7948	SSATD	14A-CLINOCHLORE	32.4618	SSATD
ANTHOPHYLLITE	29.2913	SSATD	MERVINITE	-9.4856	
MONTICELLITE	1.8186	SSATD	ACKERMANITE	-1.8642	
KA-NONTRONITE	11.6887	SSATD	K-NONTRONITE	11.1249	SSATD
CROSSULAR	12.8848	SSATD	ALBITE	4.8162	SSATD
PARASITE	26.8818	SSATD	ORDERED EPIDOTE	21.8296	SSATD
ANDRADITE	16.6888	SSATD	CA-NONTRONITE	13.3417	SSATD
MG-NONTRONITE	13.4345	SSATD	M-NONTRONITE	11.8364	SSATD
CRISTOBEALITE	-0.8536		DISORDERED DOLOM	2.4838	SSATD
ORDERED DOLOMITE	3.8723	SSATD	EPIDOTE	21.1856	SSATD
PD-OXYANNITE	19.6567	SSATD	VAIRAKITE	11.3485	SSATD
LAUMONTITE	11.3861	SSATD	MARGARITE	17.1498	SSATD
FLUORITE	-6.4979		SILLIMANITE	4.1817	SSATD
KALSILITE	.1887	SSATD	JADEITE	.3889	SSATD
CA-AL PYROXENE	.9215	SSATD	PSEUDOMOLLASTONITE	-0.7183	
CAS1205.2N2O	-7.1782		CA2S1208.6/ZH2O	-7.9533	
LAUSONITE	8.6957	SSATD	TRIDYHITE	.3887	SSATD

----- SUMMARY OF GAS SPECIES -----

GAS	LOG FUGACITY	FUGACITY	PARTIAL PRESSURE
CO2(G)	.12895	1.348712E+88	
O2(G)	-0.91896	1.285146E-81	
S2(G)	-118.93248	1.168281-116	
CH4(G)	-74.88289	1.389589E-75	
H2(G)	-19.77115	1.693746E-28	
H2S(G)	-71.37229	4.243331E-72	
STEAM	1.82927	3.382736E-81	

----- NO FURTHER INPUT FOUND -----

6.3. REACTION PATH CALCULATIONS

Reaction path calculations are considerably longer than "single point" thermodynamic calculations, essentially because they involve sequences of such calculations. The OUTPUT files are typically several thousand lines long. The results of such calculations are therefore generally best presented graphically. In the examples that follow, the results will be presented by showing parts of the OUTPUT files and also by graphs.

6.3.1. DISSOLUTION OF IRON IN SEA WATER AT 200°C

The first reaction path example is a simple one. Sea water (as defined by the EQ3NR INPUT file ISWMJP, Figure 6) is instantaneously heated to 200°C and reacted with iron metal. The sea water contains dissolved oxygen, an oxidizing agent. The iron is a strong reducing agent. The reaction path traces the corrosion of the iron. This calculation is done using arbitrary kinetics, so there is no time frame.

The EQ6 INPUT file for this example, IFESW, is shown in Figure 12. Iron metal is not currently on the thermodynamic data file that supports EQ6 calculations. It is therefore entered as a "special" reactant (JCODE = 2), and its composition (Fe) is entered on the INPUT file. The amount of iron is limited to 10^{-3} mole. The amount of sea water is about 1 kilogram (EQ3NR writes a PICKUP file with an amount of fluid containing exactly 1 kilogram of solvent water). The dissolution of the iron is described by a relative rate of unity ($d\xi_1/d\xi = 1$).

The precipitation of 14A-clinochlore, a chlorite mineral $[\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8]$, was suppressed by means of an NXMOD option. Otherwise, a very small amount of this mineral would precipitate at the start of the run. It was suppressed partly to illustrate the option and partly

Figure 12. The EQ6 INPUT file, IFESW.

INPUT FILE NAME= IFESW REVISED= #3/28/84 REVISOR= T.J. WOLERY

THIS RUN CALCULATES THE CONSEQUENCES OF REACTING IRON METAL WITH SEA WATER AT 288 DEG C. THE FIRST STEP IN THIS CALCULATION IS A TEMPERATURE JUMP FROM 25 DEG C, WHICH RESULTS IN SOME MINERAL PRECIPITATION. 14-A CLINOCHLORE IS NOT ALLOWED TO PRECIPITATE. IRON METAL IS NOT REPRESENTED IN THE THERMODYNAMIC DATA BASE. CONSEQUENTLY, IT IS SPECIFIED BELOW AS A "SPECIAL" REACTANT.

THE MAJOR FEATURE OF THIS RUN IS THE REDOX JUMP, WHICH OCCURS WHEN THE DISSOLVED OXYGEN (O2(AQ)) IS EFFECTIVELY EXHAUSTED BY THE REACTION WITH IRON.

THIS IS A NON-KINETIC SIMULATION. THE RELATIVE RATE OF DISSOLUTION OF THE IRON IS FIXED AT UNITY.

A "SPECIAL" REACTANT EFFECTIVELY HAS NO THERMODYNAMIC STABILITY. THEREFORE, THIS RUN STOPS WHEN EITHER THE IRON IS EXHAUSTED OR THE NUMBER OF REACTION PROGRESS STEPS REACHES THE LIMIT, KSTPMX.

```

NMODL1= 2
TEMPCB= 288.      JTEMP= 8
TK1= 8.      TK2= 8.      TK3= 8.
Z1STRT= 8.      ZIMAX= 1.
TSTRT= 8.      TIMEMX= 8.
KSTPMX= 258      CPLIM= 8.
DZIPR= 1.E+5      DZPRLG= 8.5      KSPPMX= 28
IFILE= 68
IOPT1-18= 8 8 8 8 8 8 8 8 8 8 8
11-28= 8 8
IOPR1-18= 8 8 8 8 8 8 8 8 8 8
IODB1-18= 8 8 8 8 8 8 8 8 8 8
11-28= 8 8
NXOPT= 8
NRCT= 1
-----
REACTANT= IRON
JCODE= 2      JREAC= 8
MORR= 8.881      MODR= 8.
VREAC= 7.892
* THE ELEMENTAL COMPOSITION OF IRON FOLLOWS
FE 1.8
ENDIT.
NSK= 8      SK= 8.      FK= 8.
NRK= 8
RK1= 1.8      RK2= 8.      RK3= 8.
-----
DLZIDP= 8.      TOLDL= 8.      TOLX= 8.
TOLBT= 8.      TOLSST= 8.
TOLSAT= 8.

```

Figure 12. The EQ6 INPUT file, IFESW (Continued).

```

SCREW1=      B.   SCREW2=      B.   SCREW3=      B.
SCREW4=      B.   SCREW5=      B.
ZKLOGU=      B.   ZKLOGL=      B.
DLZMX1=      B.   DLZMX2=      B.
    
```

```

-----
* PICKUP FILE WRITTEN BY EQ3NR.3238U52
* SUPPORTED BY EQLIB.3238U82
INPUT FILE NAME= ISWMPJ      CREATED= 83/19/84      CREATOR= T.J. VOLERY
    
```

SEA WATER TEST CASE. MAJOR CATIONS AND ANIONS, PLUS SILICA, ALUMINUM, AND IRON. THIS IS AN EXTENSION OF THE CLASSIC SEA WATER 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.

THERE IS NO FORCED ELECTRICAL BALANCING IN THIS RUN.

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. 268, 57-66.

```

UACON= CL-
TEMPC1= 2.58888E+01
NXMOD= 2
SPECIES= 14A-CLINOCHLORE      OPTION= -1      XLKMOD= B.
TYPE= 1
SPECIES= PD-OXYANNITE        OPTION= -1      XLKMOD= B.
TYPE= 1
NFFG= 8
KCT= 12                      KMT= 15        KXT= 15
KDIM= 15                    KPRS= 8
O      5.562989234468153E+01
NA     4.683775554589885E-01
K      1.828768325745569E-02
CA     1.828692614778471E-02
MG     5.314955778417717E-02
AL     7.412348973388611E-08
SI     7.123368628453687E-05
H      1.118285888286275E+02
C      2.899888585462143E-03
CL     5.458776488282518E-01
S      2.823294259718223E-02
FE     3.581212956827398E-08
ELECTR 7.938199721686357E-04
    
```

Figure 12. The EQ6 INPUT file, IFESW (Continued).

H2O	H2O	1.744365733541414E+00
NA+	NA+	-3.466514237287868E-01
K+	K+	-1.998455029378910E+00
CA++	CA++	-2.843192907349521E+00
MG++	MG++	-1.334637711162529E+00
AL+++	AL+++	-1.697853675564238E+01
SiO2(AQ)	SiO2(AQ)	-4.174261919974839E+00
H+	H+	-8.125147876090978E+00
HCO3-	CO3--	-2.816064573883779E+00
CL-	CL-	-2.728921466500633E-01
SO4--	SO4--	-1.834119181985116E+00
FE++	FE++	-1.346032643998000E+01
O2(G)	O2(G)	-1.642993298220233E+01
XISTEO		-2.629046940568411E-01
XI		-1.932703489001915E-01

because it was thought that allowing it to form merely cluttered up the example.

This run required 44.74 seconds (CPU = 43.40 seconds) to run on a CDC 7600 computer. The calculation terminated after 177 reaction-progress steps. The run ended at this point because the reactant iron was exhausted.

Parts of the OUTPUT file are shown in Figure 13. Figure 13(a) shows the printout of the state of the system at $\xi = 0$. Note that heating to 200°C resulted in the precipitation of hematite (Fe_2O_3), magnesite (MgCO_3), and anhydrite (CaSO_4). Note also the small supersaturation with respect to 14A-clinochlore.

The code's behavior in the region of the principal feature of this run, the sudden plunge in the oxygen fugacity, is shown in Figure 13(b). The "ZLG1" printed here indicates the most rapidly changing master variable. In this part of the figure, the logarithmic mass of hematite is most rapidly changing ("ZLG1(HEMATITE) = "), but this then switches to the logarithm of the oxygen fugacity ("ZLG1(O2(G)) = "). This variable plunges from -2.7803 at step 72 to -37.7244 at step 73, over an increment of reaction progress of 1.1207×10^{-5} moles. The Newton-Raphson calculation at step 72 required 24 iterations, much more than the calculations at nearby points. Actually, the behavior shown here is somewhat abnormal, because EQ6 did not have to enter the redox scan mode (Section 7.7) to deal with this redox jump.

The calculation ends at $\xi = 10^{-3}$ moles, ^{step 177} because the iron has been entirely consumed, as is shown in Figure 13(c), which gives the state of the system at the final "print point." The solution is still somewhat supersaturated with respect to 14A-clinochlore. Magnesite and anhydrite are still present. Hematite, which was present initially in a very small quantity at 200°C, is a major corrosion product, along with pyrite (FeS_2). The solution is quite reducing. Note the high concentration of $\text{H}_2\text{S}_{(\text{aq})}$ (7.7×10^{-4} molal).

Figure 13. The EQ6 OUTPUT file, OFESW. (a) The state of the system at the start of the run.

($\xi=0$)

16 8 NEMATITE
17 16 MAGNESITE
18 19 ANHYDRITE

ITER = 12

REACTION PROGRESS = 0.
LOG OF REACTION PROGRESS = -622.222222
TEMPERATURE = 222.222 DEGREES C
TOTAL PRESSURE = 18.549 BARS
COMPUTING UNITS REMAINING = 0.222

CHANGE OR ATTEMPTED CHANGE IN THE PHASE ASSEMBLAGE
START OR RE-START OF RUN

----- REACTANT SUMMARY -----

REACTANT	MOLES LEFT	MOLES DESTROYED	GRAMS LEFT	GRAMS DESTROYED
IRON	1.22222E-03	0.	6.66478E-02	0.

TOTAL MASS DESTROYED = 0. GRAMS
TOTAL MASS REMAINING = 6.66478E-02 GRAMS
TOTAL VOLUME OF DESTROYED SOLID REACTANT(S) = 0.22222 CC

REACTANT	AFFINITY	REL. RATE
IRON	0.22222	1.22222E-03

TOTAL AFFINITY EXCLUSIVE OF REACTIONS WITH NO THERMODYNAMIC DATA = 0.222 KCAL

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	6.62249E+05	6.669847E+01	6.669838E+01
NA	1.841333E+04	4.603783E-01	4.603776E-01
K	3.859614E+02	1.822778E-02	1.822766E-02
CA	1.328458E+02	3.427359E-03	3.427353E-03
MG	1.223599E+03	5.225776E-02	5.225767E-02
AL	1.934111E+03	7.412362E-02	7.412349E-02
SI	1.934785E+02	7.123373E-03	7.123361E-03
H	1.882138E+05	1.118227E+02	1.118225E+02
C	1.177747E+01	1.827919E-03	1.827917E-03
CL	1.871574E+04	5.458786E-01	5.458776E-01
S	6.626669E+02	2.137341E-02	2.137337E-02

Figure 13. The EQ6 OUTPUT file, OFESW. (a) The state of the system at the start of the run (Continued).

```

FE          1.673189E-07      3.898841E-12      3.898836E-12
CO3--      1.887919E-03      1.887917E-03
SO4--      2.137341E-02      2.137337E-02
S--        7.648677E-02      7.648664E-02
    
```

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

```

OXYGEN FUGACITY = 1.86791E-01
LOG OXYGEN FUGACITY = -.72864
EH = .72747 VOLTS
PE = 7.83685
    
```

```

PH = 8.25689
ACTIVITY OF WATER = .98243
LOG ACTIVITY OF WATER = -.01757
ALKALINITY = 8.          EQUIV/KG SOLVENT (NOT DEF. FOR T.CT.SF C)
    
```

```

IONIC STRENGTH = 8.667761E-01 MOLAL
EQUIV. STOICH. IONIC STRENGTH = 8.488786E-01 MOLAL
    
```

```

MASS OF SOLUTION = 1.834849 KG
MASS OF SOLVENT = .999996 KG
MASS OF SOLUTES = .834851 KG
CONC OF SOLUTES = 3.292976 PER CENT (W/W)
    
```

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG 6	LOG ACT
H2O	8.86892E-01	9.99998E-02				
NA+	4.42862E-01	1.01638E-01	4.42862E-01	-.36452	-.26362	-.61813
K+	9.92496E-03	3.88846E-01	9.92497E-03	-2.88327	-.38737	-2.31064
CA++	3.19998E-03	1.28252E-01	3.19998E-03	-2.49486	-.89336	-3.38823
MG++	3.44648E-02	8.97667E-01	3.44649E-02	-1.46262	-.73521	-2.19783
AL+++	8.43449E-14	2.27878E-12	8.43446E-14	-13.87394	-1.85164	-14.62678
SiO2(AQ)	7.12258E-05	4.27951E-03	7.12258E-05	-8.14736	8.88888	-4.14736
H+	8.74721E-06	8.81698E-06	8.74722E-06	-8.85814	-.14878	-8.28689
CO3--	6.75874E-18	4.88125E-08	6.75875E-18	-9.17885	-1.86382	-18.23367
CL-	8.28864E-01	1.84662E-01	8.28865E-01	-.28327	-.38737	-.59864
SO4--	2.84981E-03	1.96987E-01	2.84981E-03	-2.58829	-1.13429	-3.82267
FE++	1.81985E-17	1.81889E-18	1.81985E-17	-16.74818	-.89336	-17.63382
O2(AQ)	2.81848E-04	6.44934E-03	2.81849E-04	-3.69562	.85298	-3.64264
H2(AQ)	1.81425E-26	3.85272E-26	1.81425E-26	-25.81988	.85298	-25.76683
HS-	7.64866E-02	2.52926E-08	7.64867E-02	-81.11641	-.28396	-81.48837
FE+++	9.84978E-21	6.58876E-19	9.84971E-21	-28.88558	-1.55184	-21.55842
HCO3-	6.26785E-05	3.82446E-03	6.26786E-05	-4.28288	-.24578	-4.44866
OH-	1.83633E-06	3.12385E-06	1.83633E-06	-6.73685	-.28396	-6.82821
AL(OH)++	1.27183E-08	5.59112E-07	1.27183E-08	-7.89584	-.89336	-8.78921
AL(OH)4-	6.14131E-08	5.83492E-06	6.14132E-08	-7.21174	-.26362	-7.47536
KCL	1.88821E-04	1.17886E-02	1.88822E-04	-3.88128	8.88888	-3.88128
KSO4-	1.24786E-04	1.68547E-02	1.24786E-04	-3.98411	-.28396	-4.18827
NaCl	2.48538E-02	1.45253E-08	2.48538E-02	-1.68461	8.88888	-1.68461
NaCO3-	1.78878E-09	1.41827E-07	1.78878E-09	-8.76731	-.24578	-9.81389
NaSO4-	1.46188E-03	1.74823E-01	1.46181E-03	-2.83511	-.25264	-3.88775
CaCO3	2.88775E-09	2.89286E-07	2.88776E-09	-8.88788	8.88888	-8.88788
CaHCO3-	2.36459E-06	2.35853E-04	2.3646E-06	-6.62624	-.22419	-6.85843
CaSO4	2.24767E-04	3.85994E-02	2.24768E-04	-3.64827	8.88888	-3.64827

Figure 13. The EQ6 OUTPUT file, OFESW. (a) The state of the system at the start of the run (Continued).

MCCO3	1.77581E-08	1.69726E-06	1.77581E-08	-7.75868	0.00000	-7.75868
MCMCO3-	2.84224E-05	1.74248E-03	2.84224E-05	-4.68989	-2.26362	-4.95351
MCSO4	1.74634E-02	2.18195E-01	1.74634E-02	-1.75787	0.00000	-1.75787
M3S1O4-	0.00626E-09	7.69268E-07	0.00626E-09	-0.09225	-2.26362	-0.35587
MSO4-	4.89817E-05	4.74678E-03	4.89817E-05	-4.31858	-2.26362	-4.57429
MZCO3	9.22429E-04	5.72137E-02	9.22429E-04	-3.23587	0.00000	-2.98289
NCL	1.32851E-06	4.84388E-05	1.32851E-06	-5.87663	0.00000	-5.87663
MG(OH)-	1.09829E-04	4.58428E-03	1.09829E-04	-3.96246	-2.26362	-4.22688
CA(OH)-	3.22762E-07	1.84255E-05	3.22762E-07	-6.49112	-2.26362	-6.75473
NAOH	1.28479E-07	5.13877E-06	1.28479E-07	-6.89117	0.00000	-6.89117

----- SUMMARY OF SOLID PRODUCT PHASES-----

PRODUCT	LOG MOLES	MOLES	GRAMS	VOLUME, CC
HEMATITE	-7.7478374	1.79845E-08	3.85921E-06	5.42841E-07
MAGNESITE	-2.9618238	1.09188E-03	9.28618E-02	3.85924E-02
ANHYDRITE	-2.1637829	6.85957E-03	9.33849E-01	3.15129E-01

	MASS, GRAMS	VOLUME, CC
CREATED	1.028912E-01	3.487217E-01
DESTROYED	0.	0.
NET	1.028912E-01	3.487217E-01

WARNING-- THESE VOLUME TOTALS MAY BE INCOMPLETE

----- MINERAL SATURATION STATE SUMMARY -----

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
CORUNDUM	-7.3641		HEMATITE	0.0000	SATD
BRUCITE	-2.9684		GIBBSITE	-3.8748	
MALITE	-8.2946		EVLVITE	-8.9959	
CALCITE	-3.9581		MAGNESITE	0.0000	SATD
DOLOMITE	-1.8728		ANHYDRITE	0.0000	SATD
GYPHUM	-2.6558		QUARTZ	-3.7245	
14A-AMESITE	-1.4426		NEPHELINE	-9.7388	
ANALCIME	-9.9651		CHRYSOTILE	-1.9544	
TALC	-5.2818		ENSTATITE	-3.6592	
KYANITE	-8.9746		FORSTERITE	-5.1558	
HUNTITE	-5.9138		AMORPHOUS SILICA	-5.8542	
PHLOGOPITE	-4.8298		ARAGONITE	-4.3156	
NA-SAPONITE	-3.8588		K-SAPONITE	-4.6861	
SPINEL	-9.2541		DIASPORE	-2.2638	
CA-SAPONITE	-3.1351		BOEMMITE	-2.8553	
CHALCEDONY	-4.8945		MG-SAPONITE	-2.2781	
7A-CLINOCLORE	-5.2593		ANDALUSITE	-9.9618	
M-SAPONITE	-4.8946		14A-CLINOCLORE	0.227	SSATD
CRISTOBALITE	-4.3852		DISORDERED DOLOM	-3.4946	
ORDERED DOLOMITE	-1.8686		TRIDYMITE	-3.9386	

Figure 13. The EQ6 OUTPUT file, OFESW. (b) The sudden drop in the oxygen fugacity.

CHALCEDONY	-4.8946	MG-SAPONITE	-2.2781
7A-CLINOCHLORE	-5.2593	ANDALUSITE	-9.9618
M-SAPONITE	-4.8946	14A-CLINOCHLORE	.3287
CRISTOBALITE	-4.3852	DISORDERED DOLOM	-3.4946
ORDERED DOLOMITE	-1.6686	TRIDYMIT	-3.9388
		SSATD	

```

-----
 STEPPING TO...(NORD = 6)... ZI = 1.1888E-84, DELZI = 1.4481E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 65, ITER = 3, NCCORR = 8, ZLG1(HEMATITE ) = -4.2568
 STEPPING TO...(NORD = 6)... ZI = 1.2784E-84, DELZI = 1.6686E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 66, ITER = 3, NCCORR = 8, ZLG1(HEMATITE ) = -4.1993
 STEPPING TO...(NORD = 6)... ZI = 1.4669E-84, DELZI = 1.9167E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 67, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -1.8716
 STEPPING TO...(NORD = 6)... ZI = 1.6873E-84, DELZI = 2.2833E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 68, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -1.1579
 STEPPING TO...(NORD = 6)... ZI = 1.9487E-84, DELZI = 2.8342E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 69, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -1.2649
 STEPPING TO...(NORD = 6)... ZI = 2.2322E-84, DELZI = 2.9147E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 70, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -1.4998
 STEPPING TO...(NORD = 6)... ZI = 2.4782E-84, DELZI = 2.4687E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 71, ITER = 4, NCCORR = 8, ZLG1(O2(G) ) = -1.8377
 STEPPING TO...(NORD = 6)... ZI = 2.6635E-84, DELZI = 1.6527E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 72, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -2.7883
 STEPPING TO...(NORD = 6)... ZI = 2.7786E-84, DELZI = 1.1287E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 73, ITER = 24, NCCORR = 8, ZLG1(O2(G) ) = -37.7244
 STEPPING TO...(NORD = 6)... ZI = 2.7763E-84, DELZI = 7.1886E-85, TIME = 8. D. DLTIME = 8. D
 STEPS = 74, ITER = 6, NCCORR = 8, ZLG1(O2(G) ) = -37.7262
 STEPPING TO...(NORD = 4)... ZI = 2.7784E-84, DELZI = 2.1326E-87, TIME = 8. D. DLTIME = 8. D
 STEPS = 75, ITER = 4, NCCORR = 8, ZLG1(O2(G) ) = -37.7314
 STEPPING TO...(NORD = 5)... ZI = 2.7848E-84, DELZI = 6.3977E-87, TIME = 8. D. DLTIME = 8. D
 STEPS = 76, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.7462
 STEPPING TO...(NORD = 6)... ZI = 2.7975E-84, DELZI = 1.2724E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 77, ITER = 4, NCCORR = 8, ZLG1(O2(G) ) = -37.7738
 STEPPING TO...(NORD = 6)... ZI = 2.8888E-84, DELZI = 1.8429E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 78, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.7928
 STEPPING TO...(NORD = 6)... ZI = 2.8188E-84, DELZI = 9.9991E-87, TIME = 8. D. DLTIME = 8. D
 STEPS = 79, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.8182
 STEPPING TO...(NORD = 6)... ZI = 2.8488E-84, DELZI = 2.9997E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 80, ITER = 2, NCCORR = 8, ZLG1(O2(G) ) = -37.8565
 STEPPING TO...(NORD = 6)... ZI = 2.8766E-84, DELZI = 2.8528E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 81, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.8913
 STEPPING TO...(NORD = 6)... ZI = 2.9884E-84, DELZI = 3.1883E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 82, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.9268
 STEPPING TO...(NORD = 8)... ZI = 2.9446E-84, DELZI = 3.6212E-86, TIME = 8. D. DLTIME = 8. D
 STEPS = 83, ITER = 3, NCCORR = 8, ZLG1(O2(G) ) = -37.9568

```

Figure 13. The EQ6 OUTPUT file, OFESW. (c) The state of the system at the end of the run.

ENSTATITE	-3.4189		DIOPSIDE	-9.7439
FORSTERITE	-4.6795		FAVALITE	-9.8243
MUNTITE	-5.9839		AMORPHOUS SILICA	-8.8642
14A-RIPIDOLITE	-7.1328		PHLOGOPITE	-3.7563
FERROUS OXIDE	-5.4273		ARAGONITE	-4.3865
KA-SAPONITE	-2.8829		K-SAPONITE	-3.8592
SPINEL	-9.1485		DIASPORE	-2.3326
CA-SAPONITE	-2.3868		SOENMITE	-2.9348
CHALCEDONY	-4.8945		MG-SAPONITE	-1.6233
7A-CLINOCLORE	-4.1812		N-SAPONITE	-3.8879
14A-CLINOCLORE	1.3988	SSATD	CRISTOBALITE	-4.3853
DISORDERED DOLOM	-3.4855		ORDERED DOLOMITE	-1.8596
FERROSILITE	-7.8662		TRIDYMIT	-3.9388

STEPPING TO...(INORD = 6)... ZI = 8.4812E-04. DELZI = 6.6674E-05. TIME = 8. D. DLTIME = 8. B
 STEPS = 175. ITER = 3. NCCORR = 8. ZLG1(PYRITE)) = -3.9918

STEPPING TO...(INORD = 6)... ZI = 9.1688E-04. DELZI = 7.6686E-05. TIME = 8. D. DLTIME = 8. B
 STEPS = 176. ITER = 3. NCCORR = 8. ZLG1(PYRITE)) = -3.9311

STEPPING TO...(INORD = 6)... ZI = 1.8888E-03. DELZI = 8.3186E-05. TIME = 8. D. DLTIME = 8. B
 STEPS = 177. ITER = 3. NCCORR = 8. ZLG1(PYRITE)) = -3.8736

REACTION PROGRESS = 1.8888888888888888E-03
 LOG OF REACTION PROGRESS = -3.88888888

TEMPERATURE = 287.888 DEGREES C
 TOTAL PRESSURE = 15.849 BARS

COMPUTING UNITS REMAINING = 8.888

STEP SIZE IS LIMITED BY THE PRINT REQUIREMENT
 STEP SIZE IS LIMITED BY EXHAUSTION OF THE FOLLOWING REACTANT(S).....
 IRON

----- REACTANT SUMMARY -----

REACTANT	MOLES LEFT	MOLES DESTROYED	GRAMS LEFT	GRAMS DESTROYED
IRON	8.	1.88888E-03	8.	8.88478E-02

TOTAL MASS DESTROYED = 8.88478E-02 GRAMS
 TOTAL MASS REMAINING = 8. GRAMS
 TOTAL VOLUME OF DESTROYED SOLID REACTANT(S) = .82729 CC

Figure 13. The EQ6 OUTPUT file, OFESW. (c) The state of the system at the end of the run (Continued).

```

REACTANT      AFFINITY      REL. RATE
IRON          552.5552      1.555552E-08
TOTAL AFFINITY EXCLUSIVE OF REACTIONS WITH NO THERMODYNAMIC DATA =      5.555 KCAL
    
```

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	8.682592E-05	5.559621E-01	5.559636E-01
NA	1.541382E-04	4.683763E-01	4.683776E-01
K	3.859796E-02	1.822766E-02	1.822768E-02
CA	1.248741E-02	3.458889E-03	3.458899E-03
MG	1.217826E-03	5.177544E-02	5.177559E-02
AL	1.924282E-03	7.412329E-08	7.412349E-08
SI	1.934846E-02	7.123341E-05	7.123361E-05
H	1.582181E-05	1.118282E-02	1.118285E-02
C	8.431265E-02	7.258269E-04	7.258289E-04
CL	1.871663E-04	5.458761E-01	5.458776E-01
S	6.553797E-02	2.113728E-02	2.113733E-02
FE	2.131642E-03	3.946695E-08	3.946709E-08
CO3--		7.258269E-04	7.258289E-04
SO4--		2.113665E-02	2.113671E-02
S--		6.274544E-07	6.274561E-07

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

OXYGEN FUGACITY = 5.98848E-39
LOG OXYGEN FUGACITY = -38.22546
EM = -.17963 VOLTS
PE = -1.91343

PH = 5.28216
ACTIVITY OF WATER = .98243
LOG ACTIVITY OF WATER = -.01772
ALKALINITY = 5. EQUIV/KG SOLVENT (NOT DEF. FOR T.E.T.58 C)

IONIC STRENGTH = 5.666244E-01 MOLAL
EQUIV. STOICH. IONIC STRENGTH = 5.458761E-01 MOLAL

MASS OF SOLUTION = 1.834887 KC
MASS OF SOLVENT = 1.833993 KC
MASS OF SOLUTES = .000894 KC
CONC OF SOLUTES = 3.287971 PER CENT (W/W)

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG C	LOG ACT
H2O	5.55955E-01	1.00000E-03				
NA+	4.68274E-01	1.01633E-01	4.42873E-01	-.35451	-.26361	-.61811
K+	9.92618E-03	3.88793E-01	9.92612E-03	-2.87322	-.38735	-2.31857
CA++	3.23173E-03	1.29526E-01	3.23172E-03	-2.49257	-.89332	-3.38389
MG++	3.43825E-02	8.35618E-01	3.43824E-02	-1.46369	-.73516	-2.19887

Figure 13. The EQ6 OUTPUT file, OFESW. (c) The state of the system at the end of the run (Continued).

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
PYRRHOTITE	-4.6531		PYRITE	-.8555	SATD
ANTIGORITE	-3.2444		MAGNETITE	-1.2246	
CORUNDUM	-7.5545		HEMATITE	5.8555	SATD
BRUCITE	-2.6367		GIBBSITE	-2.1692	
MALITE	-5.2945		SYLVITE	-8.9967	
CALCITE	-3.9465		MAGNESITE	5.8555	SATD
SIDERITE	-5.4176		DOLOMITE	-1.8611	
ANHYDRITE	-.8555	SATD	GYPSUM	-2.6555	
QUARTZ	-3.7248		14A-AMESITE	-.5285	
NEPHELINE	-3.6782		ANALCIME	-9.8972	
CHRYSOTILE	-.8823		TALC	-4.2388	
ENSTATITE	-3.3353		DIOPSIDE	-9.5583	
FORSTERITE	-4.5164		FAYALITE	-9.8622	
MUNTITE	-5.9513		AMORPHOUS SILICA	-5.5542	
14A-RIPIDOLITE	-5.9218		PHLOGOPITE	-3.5886	
FEROUS OXIDE	-5.4162		ARAGONITE	-4.3848	
NA-SAPONITE	-2.5566		K-SAPONITE	-3.5127	
SPINEL	-9.1288		DIASPORE	-2.3598	
CA-SAPONITE	-2.1482		BOEMHITE	-2.9689	
CHALCEDONY	-4.2945		MG-SAPONITE	-1.2771	
7A-CLINOCLOPE	-3.8313		M-SAPONITE	-3.6558	
14A-CLINOCLOPE	1.7487	SSATD	CRISTOBALITE	-4.3853	
DISORDERED DOLOM	-3.4838		ORDERED DOLOMITE	-1.8577	
FERROSILITE	-7.5551		TRIDYHITE	-3.9368	

----- EACH REACTANT IS SATURATED OR EXHAUSTED -----

----- THE REACTION PATH HAS TERMINATED NORMALLY AT ZI = 1.85822E-03 -----

----- NO FURTHER INPUT FOUND -----

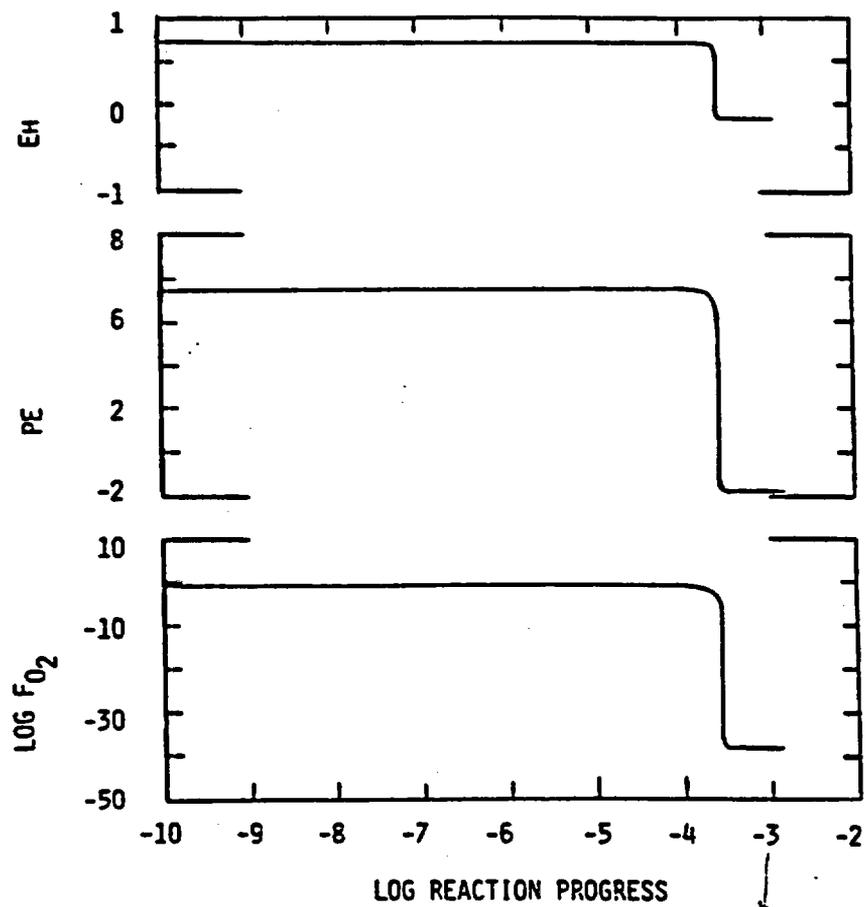
The redox behavior of the reacting system over the course of the run is shown in Figure 14, where Eh, pe, and the logarithm of the oxygen fugacity are all plotted against the logarithm of reaction progress. Recall that reaction progress in this run is equivalent to the number of moles of iron that have been dissolved. The redox drop noted above in the discussion of Figure 13(b) is the prominent feature. This phenomenon occurs when the dissolved oxygen ($O_{2(aq)}$) in the sea water is effectively exhausted by the corrosion process. This is shown in Figure 15, where pH, the logarithm of the concentration of dissolved oxygen, and the logarithm of the total concentration of dissolved iron are all plotted against the logarithm of reaction progress. At the same time, there is only a mild increase in the pH. However, the concentration of iron in solution exhibits an increase complementary to the dissolved oxygen decrease, though the new concentration is still not very high.

Figure 16 shows the masses of the minerals in equilibrium with the hot sea water as functions of reaction progress. The mass of anhydrite decreases very slightly during the run. There is also a modest increase in the mass of magnesite near the end of the run, where the pH exhibits a slight increase. The mass of hematite increases dramatically, as expected. Pyrite, the only phase to appear in the system during the run, appears just after the redox drop has occurred, and is also a major corrosion product by the end of the run.

The phase assemblage after the appearance of pyrite is not actually sufficient to fix the oxygen fugacity or redox potential, though it clearly plays a heavily influential role. The amount of sulfide dissolved in solution after the redox drop is of about the same magnitude as the amount of reduced sulfur present in pyrite. It can be said, however, that the redox state at the end of the run is dominantly controlled by the chemistry of the sulfur.

This run is an example of a purely theoretically based calculation, heavily emphasizing thermodynamic equilibrium. The "correctness" of this run depends on the accuracy of the thermodynamic data and the completeness of the data base with respect to the presence of all needed aqueous and mineral

Figure 14. Eh, pe, and log oxygen fugacity as a function of progress in the reaction of iron metal with sea water at 200°C.



0.10⁻³M Fe.

Figure 15. The pH, concentration of dissolved oxygen, and the total concentration of dissolved iron as a function of progress in the reaction of iron metal with sea water at 200°C.

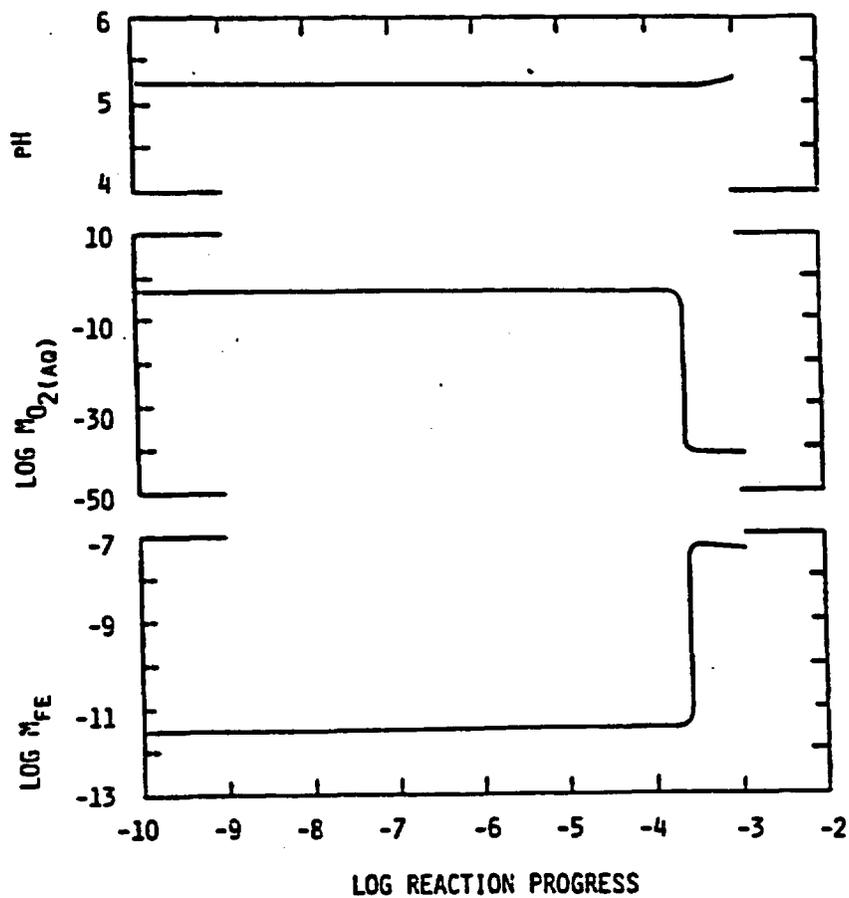
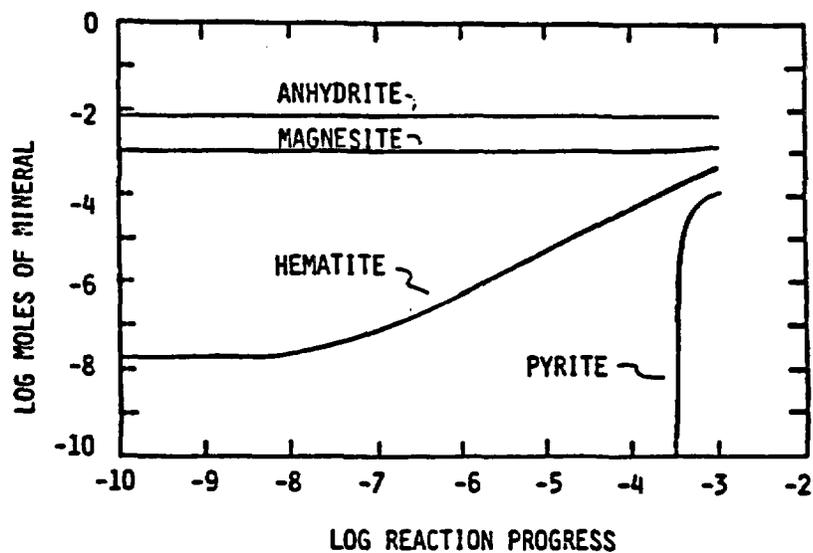


Figure 16. The logarithmic masses of minerals in equilibrium with sea water as a function of reaction progress during reaction with iron metal at 200°C.



species. However, there is a larger issue. Begging the question on these points, whether or not such calculated results such as these would be obtained in the laboratory or in the field depends largely on kinetic effects, which would require a larger assessment of the problem. Calculations such as the example here generally represent only a first cut at trying to model the behavior of real aqueous geochemical systems.

6.3.2. KINETIC DISSOLUTION OF ALBITE IN DISTILLED WATER AT 90°C AND CONSTANT CO₂ FUGACITY OF 10⁻² BAR

A fairly sophisticated example is a kinetic calculation of the dissolution of albite (sodium feldspar, NaAlSi₃O₈) in distilled water at 90°C and a constant CO₂ fugacity of 10⁻² bar. It is a model of a hypothetical laboratory experiment, one that could actually be carried out to test this model. This run was terminated when the model time exceeded one year. Kinetic calculations of this kind can actually run out to infinity however, because the code uses reaction progress, not time, as the working measure of reaction.

The EQ3NR INPUT file used to create the initial distilled water is shown in Figure 17. Note that it is not a pure water, but contains trace amounts of the components of albite. It also contains dissolved O₂ and CO₂ consistent with equilibrium with the atmosphere (fugacities of 10^{-0.68} and 10^{-3.5} bar, respectively). The pH is constrained to satisfy electrical balance. It turned out to be 5.67 (the 5.5 value on the INPUT file represents only an initial guess).

The EQ6 INPUT file for this run, IABDW2, is shown in Figure 18. The mass of albite added to the system is 50 grams (0.19068 moles). The surface area of the albite sample is taken to be 40,000 cm² (4 m²), which corresponds to a specific surface area of 800 cm²/g. This is about the same as the specific surface area as the crushed albite samples used by Knauss and Wolery (1984) in a series of dissolution rate experiments at 25°C and 70°C. Their albite samples were crushed and sieved to a size range of 75-125 microns and exhaustively washed in isopropanol to remove clining fine particles. The specific surface area was measured by the BET Ar method.

The dissolution rate law for albite is a one-term version of equation 3-34, a form consistent with transition state theory (see for example Aagaard and Helgeson, 1982). The form with no pH dependence was used, consistent with

Figure 17. The EQ3NR INPUT file, IDWA.

INPUT FILE NAME= IDWA REVISED= 03/19/84 REVISOR= T.J. WOLERY

DISTILLED WATER IN EQUILIBRIUM WITH CO2 AND O2 IN THE ATMOSPHERE.
 TRACES OF DISSOLVED SODIUM, SILICA, AND ALUMINUM ARE INCLUDED. THE PH IS
 CALCULATED FROM ELECTRICAL BALANCE.

```

    TEMPC=          25.
    RHO=            1.00
    FEP=           -8.68
    TOLET=          0.
    ITERMX=        0
    IOPT1-10=      0  0  0  0  0  0  0  0  0  0
    IOPR1-10=      0  0  0  0  0  0  0  0  0  0
    IODB1-10=      0  0  0  0  0  0  0  0  0  0
    UEBAL= H+
    NXMOD= 1
    SPECIES= PD-OXYANITE
    TYPE= 1
    NA+
    AL+++
    SIO2(AQ)
    H+
    HCO3-
    CO3--
    O2(AQ)
    TDSPL=          0.
    UREDOX=
    TOLDL=          0.
    UACION= NA+
    OPTION= -1
    1.E-12  0
    1.E-12  0
    1.E-12  0
    -5.50  16
    -3.5   21
    CO2(G)
    30
    27
    ENDIT.
    
```

Figure 18. The EQ6 INPUT file, IABDW2.

INPUT FILE NAME= IABDW2 REVISED= 03/19/84 REVISOR= T.J. WOLERY

THIS IS A KINETIC REACTION PATH CALCULATION OF THE DISSOLUTION OF PURE ALBITE AT 90 DEG C IN DISTILLED WATER UNDER A FIXED FUGACITY OF 0.01 BAR CO₂. THIS RUN MODELS A HYPOTHETICAL LABORATORY EXPERIMENT IN WHICH A CO₂-BEARING GAS MIXTURE IS BUBBLED THROUGH AN AUTOCLAVE.

THE MASS OF ALBITE IN THIS RUN IS 50 GRAMS. THE MASS OF AQUEOUS SOLUTION IS 1 KG. CRUSHED ALBITE SIEVED INTO THE SIZE RANGE 75-125 MICRONS HAS A BET AR SPECIFIC SURFACE AREA OF ABOUT 800 CM²/G (KNAUSS AND WOLERY, 1984). THE TOTAL SURFACE AREA IS THEREFORE 40000 CM². THIS RUN USES THE TRANSITION STATE RATE LAW FOR THE MID-PH RANGE AND A RATE CONSTANT OF 2.5E-15 MOL/CM²/S (CONSISTENT WITH BET AR SURFACE AREA), AN EXTRAPOLATION OF KNAUSS AND WOLERY'S (1984) 8.1E-16 MOL/CM²/S MEASUREMENT AT 70 DEG C AND ASSUMING AN ACTIVATION ENERGY OF 14 KCAL.

THIS RATE LAW DOES NOT TAKE INTO ACCOUNT ENHANCED INITIAL RATES DUE TO THE PRESENCE OF DISTURBED MATERIAL ON THE SURFACE OF THE ALBITE. TO CARRY OUT A MATCHING EXPERIMENT, THE ALBITE SAMPLE WOULD HAVE TO BE PRE-TREATED (I.E., BY COOKING IN DISTILLED WATER FOR SEVERAL DAYS).

THE FOLLOWING PHASES ARE NOT ALLOWED TO PRECIPITATE- PARAGONITE (SODIUM MICA), PYROPHYLLITE, QUARTZ, TRIDYMIT, CHALCEDONY, AND CRISTOBALITE.

REFERENCE

KNAUSS, K.G., AND WOLERY, T.J. 1984. DEPENDENCE OF ALBITE DISSOLUTION KINETICS ON PH AND TIME. MANUSCRIPT IN PREPARATION FOR SUBMISSION TO GEOCHIMICA ET COSMOCHEMICA ACTA.

```

NMODL1= 2
TEMPCE= 90.      JTEMP= 0
TK1= 0.      TK2= 0.      TK3= 0.
ZISTR1= 0.      ZIMAX= 1.
TSTR1= 0.      TIMEMX= 3.15E+7
KSTPMX= 500      CPLIM= 0.
DZ1PR= 1.E+5      DZPRLG= 0.5
IFILE= 60
IOPT1-1E= 1    0    0    0    0    0    0    0    0    0
11-2E= 0    0
IOFRI-1E= 0    0    0    0    0    0    0    0    0
IODB1-1E= 0    0    0    0    0    0    0    0    0
11-2E= 0    0
NXOPT= 0
NRCT= 1
-----
REACTANT= ALBITE
JCODE= 0      JREAC= 0
MORR= 0.19068      MODR= 0.
NSK= 1      SK= 40000.      FK= 0.
NRK= 1
IMECH= 1
RK= 2.5E-15      NDACT= 0      CSIGMA= 1.
-----
DLZIDP= 0.      TOLDL= 0.      TOLX= 0.
TOLBT= 0.      TOLSST= 0.
SCREW1= 0.      SCREW2= 0.      SCREW3= 0.
SCREW4= 0.      SCREWS= 0.
ZKLOGU= 0.      ZKLOGL= 0.

```


Figure 18. The EQ6 INPUT file, IABDW2 (Continued).

C	1.24551716638237E-05
ELECTR	-1.897353881849633E-19
H2O	H2O 1.744365733541414E+00
NA+	NA+ -1.20000000000059919E+01
AL+++	AL+++ -1.312188495247790E+01
SiO2(AQ)	SiO2(AQ) -1.2000005430415177E+01
H+	H+ -5.666012906986111E+00
HCO3-	CO3-- -5.666996172064813E+00
O2(G)	O2(G) -6.799999999999997E-01
XISTEQ	-1.199999999999994E+01
XI	-5.666002719698270E+00

The necessary changes should be made a little clearer:

the pH range of this hypothetical experiment. Other terms could be added to account for rate behavior in very acid or very alkaline pH regions (see Knauss and Wolery, 1984). The rate law here can be written

$$d\xi_i/dt = f_i s_i k_i (1 - e^{-A_i/\sigma_i RT}) \quad (6-1)$$

The rate constant used here ($k_i = 2.5 \times 10^{-15}$ mol/cm²-s) is based on the measured value of Knauss and Wolery (1984) at 70°C, extrapolated to 90°C assuming an activation energy of 14 kcal.

The fugacity of CO₂ is fixed at 10⁻² bar by adding a fictive mineral with the stoichiometry of CO₂ to the system (See Delany and Wolery, 1984). This is specified by the NFFG option on the lower part of the INPUT file. (Specification of this option required a change from what EQ3NR had written on its PICKUP file.) Saturation of the system with this fictive phase was assured by adding 0.1 mole of CO₂ to the system at the start of the run ("MOFFG= 0.1").

Equilibrium precipitation of several phases was suppressed using the NXMOD option. Quartz, tridymite, chalcedony, and cristobalite (all SiO₂ polymorphs) were suppressed. Quartz, the most stable of the lot at this temperature, often does not form in similar autoclave experiments, on a time scale of months, even though the solutions are quite supersaturated. Its above polymorphs were suppressed because they would otherwise appear in its place, as demonstrated by preliminary EQ6 runs. Amorphous silica was not suppressed, but it did not appear in the run presented here.

It was expected that one of the important secondary product minerals that would form would be a sodium montmorillonite. This is really a solid solution clay mineral, but it is represented in the EQ6 data base by Na-beidellite [Na_{0.33}Al_{2.33}Si_{3.67}O₁₀(OH)₂]. Pyrophyllite [Al₂Si₄O₁₀(OH)₂], a closely related clay mineral, and paragonite [NaAl₃Si₃O₁₀(OH)₂], sodium mica, were suppressed because it was felt that they were less likely to actually form in a real experiment. It was thought that they might erroneously appear in the EQ6 run in competition with the montmorillonite,

largely because the montmorillonite is represented by a single, idealized composition, and because its thermodynamic property values are only estimates based on correlation algorithms (Wolery, 1978).

The run was set to stop when either the model time exceeded one year (TIMEMX= 3.15E+7") or 500 reaction progress steps had been taken ("KSTPMX= 500"). The run actually stopped after 378 reaction progress steps, when the model time exceeded the above limit. The run required 29.10 seconds (CPU = 27.00 seconds) on a CDC 7600 computer.

The state of the system at the start of the run is depicted by a part of the OUTPUT file shown in Figure 19(a). Besides a temperature jump from 25°C to 90°C, the initial calculation also had to deal with the addition of 0.1 moles of CO₂ and the precipitation of the fictive CO₂ mineral phase ("FIX CO2(G)"). The starting pH is then 5.21. The solution is oxidizing (Eh = 837 millivolts) due to the presence of dissolved oxygen. It stays oxidizing because albite dissolution does not consume dissolved oxygen.

The state of the system at the end of the run is shown by the part of the OUTPUT file given in Figure 19(b). Only a small fraction of the original albite has been destroyed (0.00197 moles out of the original 0.19068 moles). The surface area, which was constrained to maintain a fixed specific surface area value, has decreased from 40,000 cm² to 39,586 cm². The dissolution rate of the albite has gone down from 2.50 x 10⁻¹⁵ mol/cm²-s to 1.79 x 10⁻¹¹ mol/cm²-s. The pH has gone up from 5.21 to 7.59. It would have gone up significantly higher if not for the imposed CO₂ fugacity. At the end of the run, the only reaction product present is Na-beidellite, but the solution is supersaturated with respect to all the suppressed pure silica phases.

The behavior of the albite dissolution rate ($d\xi_1/dt$) during the run is shown in Figure 20, where this function is plotted against the logarithm of time. The rate is constant over much of the first part of the run, decreasing only when the dissolution affinity (A_d , equivalent to A_1 in equation 6-1) declines to less than a couple of kilocalories (See Figure 21). This figure

Figure 19. The EQ6 OUTPUT file, OABDW2. (a) The state of the system at the start of the run.

1 SUPERSATURATED PURE MINERALS
2 SUPERSATURATED SOLID SOLUTIONS

THE MOST SUPERSATURATED PHASES AFFINITY, KCAL
1 31 FIX CO2(G) 8.87438667

ATTEMPTED SPECIES ASSEMBLAGE NO. 2

1 1 O
2 2 NA
3 6 AL
4 7 SI
5 13 N
6 14 C
7 CHARGE BALANCE
8 KISTEO
9 XI
10 31 FIX CO2(G)

ITER = 14

REACTION PROGRESS = 8.
LOG OF REACTION PROGRESS = -582.888888

TIME = 8. SEC
 = 8. DAYS
 = 8. YEARS

LOG SEC = -582.882
LOG DAYS = -582.882
LOG YEARS = -582.882

TEMPERATURE = 98.882 DEGREES C
TOTAL PRESSURE = 1.013 BARS

COMPUTING UNITS REMAINING = 8.888

CHANGE OR ATTEMPTED CHANGE IN THE PHASE ASSEMBLAGE
START OR RE-START OF RUN

----- REACTANT SUMMARY -----

REACTANT	MOLES LEFT	MOLES DESTROYED	GRAMS LEFT	GRAMS DESTROYED
ALBITE	1.92688E-01	8.	8.88827E-01	8.

TOTAL MASS DESTROYED = 8. GRAMS

Figure 19. The EQ6 OUTPUT file, OABDW2. (a) The state of the system at the start of the run (Continued).

TOTAL MASS REMAINING = 6.22227E+01 GRAMS
 TOTAL VOLUME OF DESTROYED SOLID REACTANT(S) = 8.88888 CC

REACTANT	AFFINITY KCAL/MOL	REL. RATE MOL/MOL	ABS. RATE MOL/SEC	SURFACE AREA SQ. CM.	INTRINSIC RATE MOL/SEC/SQ. CM.
ALBITE	72.8153	1.00000E+00	1.00000E-10	4.00000E+04	2.50000E-15

TOTAL AFFINITY EXCLUSIVE OF REACTIONS WITH NO THERMODYNAMIC DATA = 72.815 KCAL

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	8.881157E+05	5.551111E+01	5.551111E+01
NA	2.298948E+08	1.00000E-12	1.00000E-12
AL	2.698119E+08	1.00000E-12	1.00000E-12
SI	2.808514E+08	1.00000E-12	1.00000E-12
H	1.118942E+05	1.118942E+02	1.118942E+02
C	1.135166E+08	9.451266E-05	9.451193E-05
CO3--		9.451266E-05	9.451193E-05
SO4--		S.	S.
S--		S.	S.

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

OXYGEN FUGACITY = 3.48411E-01
 LOG OXYGEN FUGACITY = -.45888
 EM = .03664 VOLTS
 PE = 11.61135

PH = 5.28841
 ACTIVITY OF WATER = 1.00000
 LOG ACTIVITY OF WATER = -.00000
 ALKALINITY = S. EQUIV/KG SOLVENT (NOT DEF. FOR T.CT.SR C)

IONIC STRENGTH = 6.22924E-05 MOLAL
 EQUIV. STOICH. IONIC STRENGTH = 1.00000E-12 MOLAL

MASS OF SOLUTION = 1.00000E+01 KG
 MASS OF SOLVENT = .999999 KG
 MASS OF SOLUTES = .000001 KG
 CONC OF SOLUTES = .001000 PER CENT (W/W)

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG G	LOG ACT
H2O	5.55092E+01	9.99999E+02				
NA+	1.00000E-12	2.29894E-11	1.00000E-12	-12.00000	-.00145	-12.00145
AL+++	3.44165E-15	9.26627E-15	3.44165E-15	-15.46323	-.01302	-15.47625
SiO2(AQ)	9.99857E-13	6.82754E-11	9.99857E-13	-12.00000	S.00000	-12.00000
H+	6.22926E-05	6.28854E-06	6.22927E-05	-5.20496	-.00145	-5.20841
CO3--	6.81269E-11	4.88822E-09	6.81270E-11	-10.16668	-.00501	-10.17249

Figure 19. The EQ6 OUTPUT file, OABDW2. (a) The state of the system at the start of the run (Continued).

O2(AQ)	2.63633E-04	8.43699E-03	2.63633E-04	-3.67987	.00000	-3.67987
H2(AQ)	3.85454E-06	6.16794E-06	3.85454E-06	-36.61685	.00000	-36.61685
HCO3-	6.14672E-06	3.75654E-04	6.14672E-06	-6.21136	-.00145	-6.21281
OH-	6.24677E-08	1.86137E-06	6.24677E-08	-7.28476	-.00145	-7.28621
AL(OH) \leftrightarrow	1.48381E-13	6.52362E-12	1.48381E-13	-12.82886	-.00588	-12.83474
H2CO3	8.83661E-05	5.48885E-03	8.83661E-05	-4.85372	.00000	-4.85372

----- SUMMARY OF SOLID PRODUCT PHASES-----

PRODUCT	LOG MOLES	MOLES	GRAMS	VOLUME, CC
FIX CO2(G)	-1.0003566	9.99179E-02	4.39739E-02	0.

----- GRAND SUMMARY OF SOLID PHASES (E.S.+P.R.S.-DESTROYED REACTANTS) -----

PHASE/END-MEMBER	LOG MOLES	MOLES	GRAMS	VOLUME, CC
ALBITE	-000.0000000	0.	0.	0.
FIX CO2(G)	-1.0003566	9.99179E-02	4.39739E-02	0.

	MASS, GRAMS	VOLUME, CC
CREATED	4.397389E-02	0.
DESTROYED	0.	0.
NET	4.397389E-02	0.

WARNING-- THESE VOLUME TOTALS MAY BE INCOMPLETE

----- MINERAL SATURATION STATE SUMMARY -----

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
GIBBSITE	-8.2496		DIASPORE	-8.7139	
BOENMITE	-9.6616		FIX CO2(G)	.0000	SATD

STEPPING TO...(NOXD = 0)... ZI = 1.0000E-10, DELZI = 1.0000E-10, TIME = 1.1674E-05 D, DLTIME = 1.1674E-05 D
 STEPS = 1, ITER = 6, NCCORR = 0, ZLG1(SIG2(AQ)) = -9.6218

REACTION PROGRESS = 9.99999999999984E-11
 LOG OF REACTION PROGRESS = -16.000000

TIME = 1.000E-02 SEC

Figure 19. The EQ6 OUTPUT file, OABDW2. (b) The state of the system at the end of the run.

```

STEPPING TO...(NORD = 4)... ZI = 1.9416E-#3. DELZI = 4.9384E-#6. TIME = 3.5302E-#2 D. DLTIME = 2.6110E-#7 D
STEPS = 376. ITER = 2. NCCORR = #, ZLC1IAL+++ ) = -18.5718

STEPPING TO...(NORD = 4)... ZI = 1.9486E-#3. DELZI = 6.9138E-#6. TIME = 3.5766E-#2 D. DLTIME = 3.7793E-#7 D
STEPS = 376. ITER = 2. NCCORR = #, ZLC1IAL+++ ) = -18.5777

STEPPING TO...(NORD = 5)... ZI = 1.9502E-#3. DELZI = 9.6793E-#6. TIME = 3.6316E-#2 D. DLTIME = 5.5544E-#7 D
STEPS = 377. ITER = 2. NCCORR = #, ZLC1IAL+++ ) = -18.5872

STEPPING TO...(NORD = 5)... ZI = 1.9717E-#3. DELZI = 1.3551E-#5. TIME = 3.7162E-#2 D. DLTIME = 8.3656E-#7 D
STEPS = 378. ITER = 2. NCCORR = #, ZLC1IAL+++ ) = -18.5888

```

```

-----
REACTION PROGRESS = 1.97174891218344E-#3
LOG OF REACTION PROGRESS = -2.7551484

```

```

TIME = 3.218E-#7 SEC
      = 3.715E-#2 DAYS
      = 1.817E-#2 YEARS

```

```

LOG SEC = 7.535
LOG DAYS = 2.572
LOG YEARS = .887

```

```

TEMPERATURE = 92.888 DEGREES C
TOTAL PRESSURE = 1.513 BARS

```

```

COMPUTING UNITS REMAINING = 8.888

```

MAXIMUM VALUE OF TIME

----- REACTANT SUMMARY -----

REACTANT	MOLES LEFT	MOLES DESTROYED	GRAMS LEFT	GRAMS DESTROYED
ALBITE	1.88788E-#1	1.97175E-#3	4.94836E-#1	5.17838E-#1

```

TOTAL MASS DESTROYED = 5.17838E-#1 GRAMS
TOTAL MASS REMAINING = 4.94836E-#1 GRAMS
TOTAL VOLUME OF DESTROYED SOLID REACTANT(S) = .19767 CC

```

REACTANT	AFFINITY KCAL/MOL	REL. RATE MOL/MOL	ABS. RATE MOL/SEC	SURFACE AREA SQ. CM.	INTRINSIC RATE MOL/SEC/SQ. CM.
ALBITE	.1442	1.8888E-#3	1.79285E-11	3.95864E-#4	4.52896E-16
TOTAL AFFINITY EXCLUSIVE OF REACTIONS WITH NO THERMODYNAMIC DATA =				.144 KCAL	

----- ELEMENT TOTALS FOR THE AQUEOUS PHASE -----

Figure 19. The EQ6 OUTPUT file, OABDW2. (b) The state of the system at the end of the run (Continued).

ELEMENT	MG/KG SOLN.	MOLAL CONC.	MOLES
O	8.827118E-05	8.562865E-01	8.551878E-01
NA	3.897768E-01	1.692758E-03	1.692781E-03
AL	4.844958E-02	1.499639E-06	1.499589E-06
SI	7.895868E-01	2.811987E-03	2.811893E-03
H	1.118618E-05	1.118227E-02	1.118169E-02
C	1.993165E-01	1.659984E-03	1.659928E-03
CO3--		1.659984E-03	1.659928E-03
SO4--		S.	S.
S--		S.	S.

WARNING-- CO3--, SO4--, AND S-- TOTALS REQUIRE THAT ROUTINE COMPI HAVE THE NAMES OF NON-CARBONATE CARBON, SULFIDE SULFUR, AND NON-SULFATE SULFUR AQUEOUS SPECIES

OXYGEN FUGACITY = 3.48533E-01
 LOG OXYGEN FUGACITY = -.46785
 EM = .86478 VOLTS
 PE = 9.22617

PH = 7.89364
 ACTIVITY OF WATER = .99994
 LOG ACTIVITY OF WATER = -.00003
 ALKALINITY = S. EQUIV/KG SOLVENT (NOT DEF. FOR T.GT.5E C)

IONIC STRENGTH = 1.697586E-03 MOLAL
 EQUIV. STOICH. IONIC STRENGTH = 1.692758E-03 MOLAL

MASS OF SOLUTION = 1.822288 KG
 MASS OF SOLVENT = .999966 KG
 MASS OF SOLUTES = .822322 KG
 CONC OF SOLUTES = .832146 PER CENT (W/W)

SPECIES	MOLES	GRAMS	CONC	LOG CONC	LOG G	LOG ACT
H2O	8.55274E-01	9.99966E-02				
NA+	1.69259E-03	3.89127E-02	1.69268E-03	-2.77143	-.82274	-2.79418
AL+++	2.81184E-19	6.77745E-18	2.81192E-19	-18.89999	-.19249	-18.79249
SiO2(AQ)	2.71317E-03	1.83218E-01	2.71326E-03	-2.56651	S.82222	-2.56651
H+	2.67714E-08	2.69856E-08	2.67723E-08	-7.57231	-.82132	-7.59364
CO3--	4.88133E-06	2.92924E-04	4.88149E-06	-5.31145	-.89559	-5.48284
O2(AQ)	2.63633E-04	8.43599E-03	2.63642E-04	-3.57899	.82214	-3.57885
H2(AQ)	3.85275E-36	6.15435E-36	3.85285E-36	-35.51529	.82214	-35.51516
HCO3-	1.56661E-03	9.55971E-02	1.56667E-03	-2.80582	-.82259	-2.82762
OH-	1.59174E-05	2.72785E-04	1.59188E-05	-4.79811	-.82292	-4.82181
AL(OH)4--	2.18441E-14	9.25777E-13	2.18448E-14	-13.67686	-.82274	-13.76569
AL(OH)3	1.49959E-06	1.42477E-04	1.49964E-06	-5.52481	-.82274	-5.84676
NaCO3-	1.82982E-07	8.54742E-06	1.82986E-07	-6.59722	-.82259	-7.82832
H2SiO4-	9.87285E-05	9.38984E-03	9.87241E-05	-4.80558	-.82274	-4.82832
H2CC3	8.8329E-05	5.4786E-03	8.8331E-05	-4.85388	.82214	-4.85374
NaOH	8.39221E-09	2.85689E-07	8.39243E-09	-8.19447	S.82222	-8.19447

----- SUMMARY OF SOLID PRODUCT PHASES-----

Figure 19. The EQ6 OUTPUT file, OABDW2. (b) The state of the system at the end of the run (Continued).

PRODUCT	LOG MOLES	MOLES	GRAMS	VOLUME, CC
NA-BEIDELLITE	-3.8728347	8.45681E-#4	3.18789E-#1	1.18385E-#1
FIX CO2(G)	-1.8872148	9.83825E-#2	4.32649E-#8	#.
----- GRAND SUMMARY OF SOLID PHASES (E.S.+P.R.S.-DESTROYED REACTANTS) -----				
PHASE/END-MEMBER	LOG MOLES	MOLES	GRAMS	VOLUME, CC
NA-BEIDELLITE	-3.8728347	8.45681E-#4	3.18789E-#1	1.18385E-#1
ALBITE	-2.7851484	-1.97178E-#3	-5.17838E-#1	-1.97668E-#1
FIX CO2(G)	-1.8872148	9.83825E-#2	4.32649E-#8	#.
	MASS, GRAMS	VOLUME, CC		
CREATED	4.639283E-#8	1.183847E-#1		
DESTROYED	8.178379E-#1	1.976678E-#1		
NET	4.122248E-#8	-8.728313E-#2		

WARNING-- THESE VOLUME TOTALS MAY BE INCOMPLETE

----- MINERAL SATURATION STATE SUMMARY -----

MINERAL	AFFINITY, KCAL	STATE	MINERAL	AFFINITY, KCAL	STATE
CORUNDUM	-9.1377		DEHYDRATED ANALC	-7.7887	
GIBBSITE	-1.8697		QUARTZ	1.8355	SSATD
LOW ALBITE	-1.1442		NEPHELINE	-6.9583	
ANALCIME	-1.4985		KAOLINITE	-1.1586	
PYROPHVLLITE	.1276	SSATD	NA-BEIDELLITE	8.8888	SATD
KYANITE	-6.7524		AMORPHOUS SILICA	-1.8147	
HIGH ALBITE	-1.7624		H-BEIDELLITE	-1.9491	
PARAGONITE	-1.9346		DIASPORE	-2.3339	
SOENKITE	-3.2816		CHALCEDONY	.6664	SSATD
ANDALUSITE	-6.9831		ALBITE	-1.1442	
CRISTOBALITE	-3.178	SSATD	SILLIMANITE	-7.4144	
JADEITE	-3.8996		TRIDYHITE	.8399	SSATD
FIX CO2(G)	-.8888	SATD			

----- NO FURTHER INPUT FOUND -----

Figure 20. The rate of albite dissolution ($d\xi_1/dt$) as a function of time.

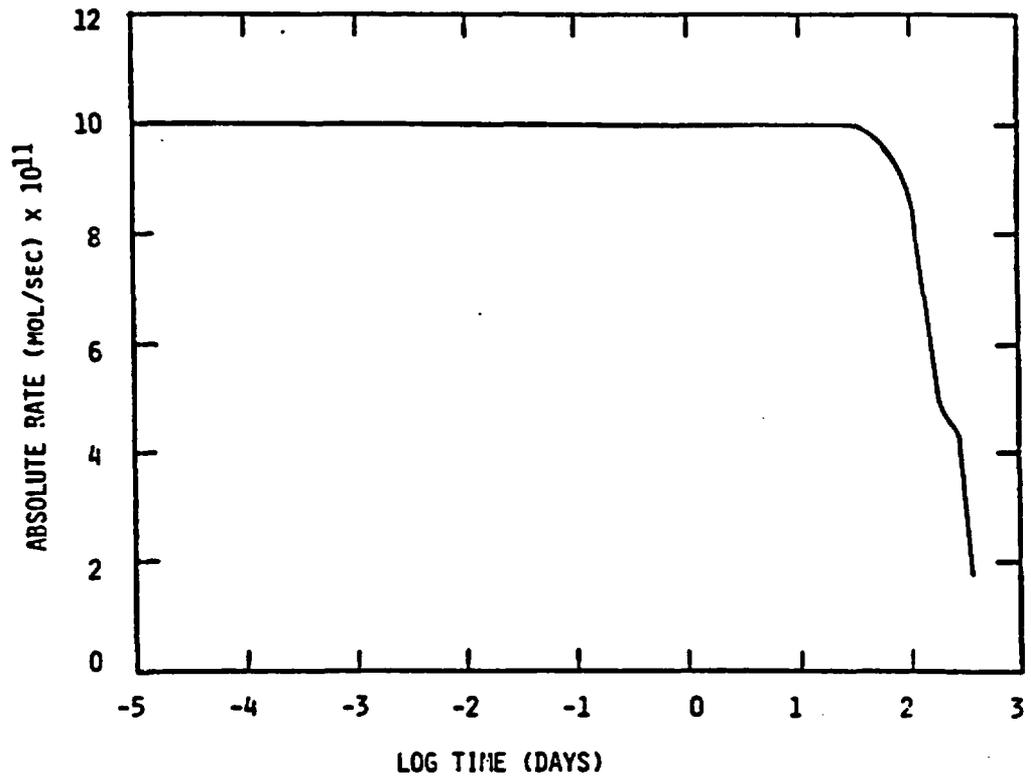
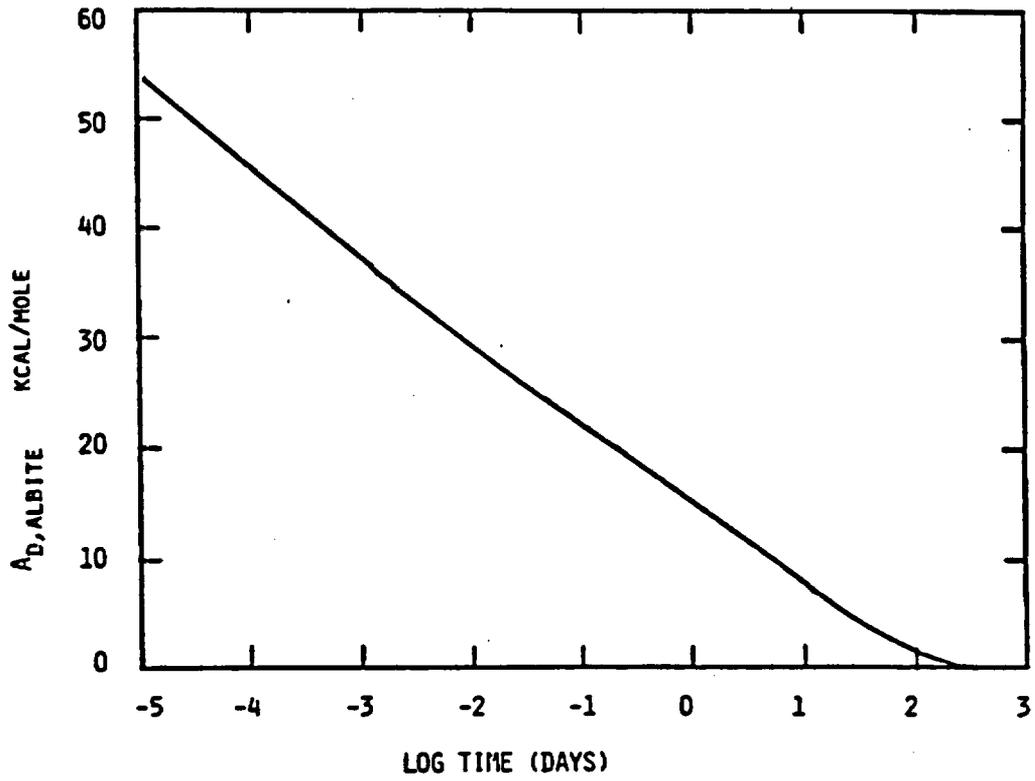


Figure 21. The affinity of albite to dissolve as a function of time.



also shows that the solution is close to equilibrium with albite [undersaturated by only 144 calories, see Figure 19(b)].

Changes in the chemistry of the solution as a function of time are depicted in Figures 22 and 23. Figure 22 shows the increases in the total concentrations of Na, Si, and Al due to the dissolution of the albite, and the increase in the total concentration of CO_2 that is due to the dissolution of the fictive CO_2 mineral required to keep the CO_2 fugacity fixed at 10^{-2} bar. Note that the chemical changes shown here indicate the apparent incongruity of the albite dissolution. Figure 23 shows the changes in p_e , Eh, and pH during the run. The changes in p_e and Eh are minor and not terribly significant in this problem. The pH shows a marked increase, as noted above, which would be even greater were it not for the buffering effect due to equilibrium with the fictive CO_2 mineral.

Figure 24 depicts the sequence of secondary minerals during the run (the fictive CO_2 mineral is ignored here). Gibbsite $[\text{Al}(\text{OH})_3]$ is the first such phase to appear. Next is kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, which competes with gibbsite as a sink for aluminum. The consequence of this competition is that the gibbsite becomes completely dissolved. A similar competitive phenomenon occurs later in the reaction when Na-beidellite $[\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2]$ appears. Kaolinite similarly disappears before the end of the run.

Figure 25 is a plot of the affinity to precipitate (A_p) for quartz, cristobalite, and paragonite. The saturation condition holds when A_p is zero, and supersaturation holds when it is positive. Quartz and cristobalite supersaturate, quartz after about ten days, cristobalite later in the run. Curves for the other suppressed pure silica phases, tridymite and cristobalite, would plot between these two. The curve for paragonite $[\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2]$ shows that it was not necessary to suppress precipitation of this phase- it would not have formed, anyway.

Figure 26 is a similar plot for gibbsite, kaolinite, and pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$. The times when gibbsite and kaolinite are present

Figure 22. Concentrations of total dissolved C, Si, Na, and Al as functions of time.

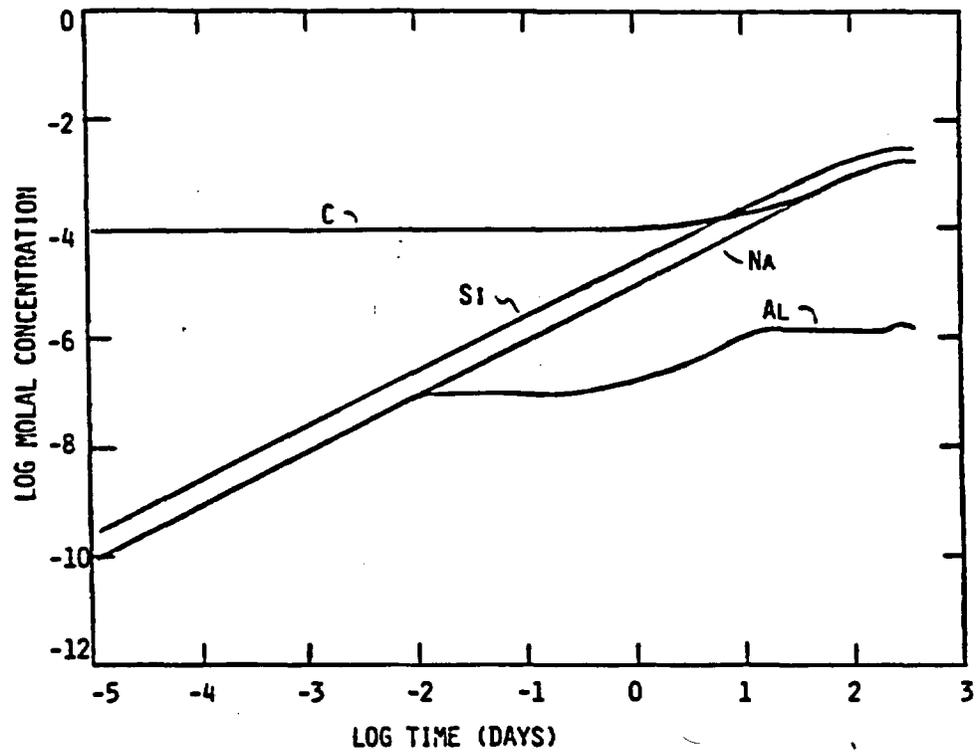


Figure 23. The pH, Eh, and pe as functions of time.

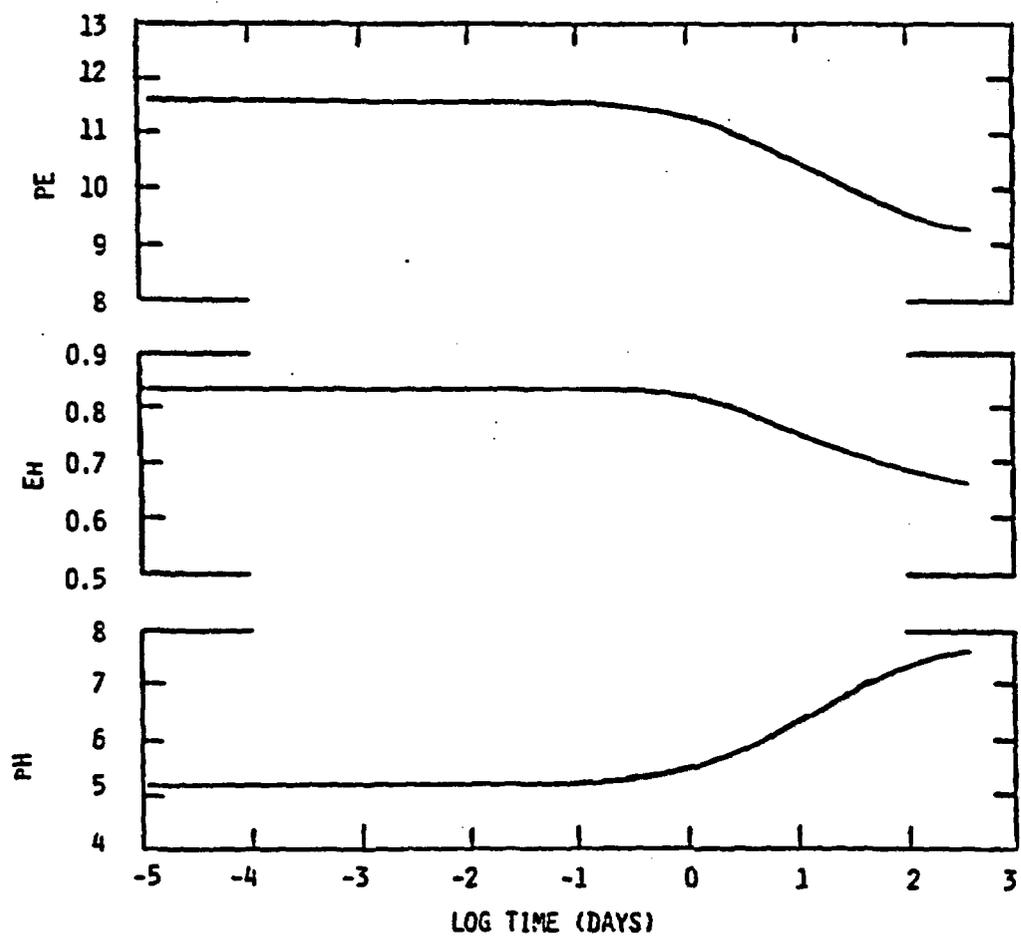


Figure 24. Logarithmic masses of minerals in equilibrium with the aqueous solution as a function of time.

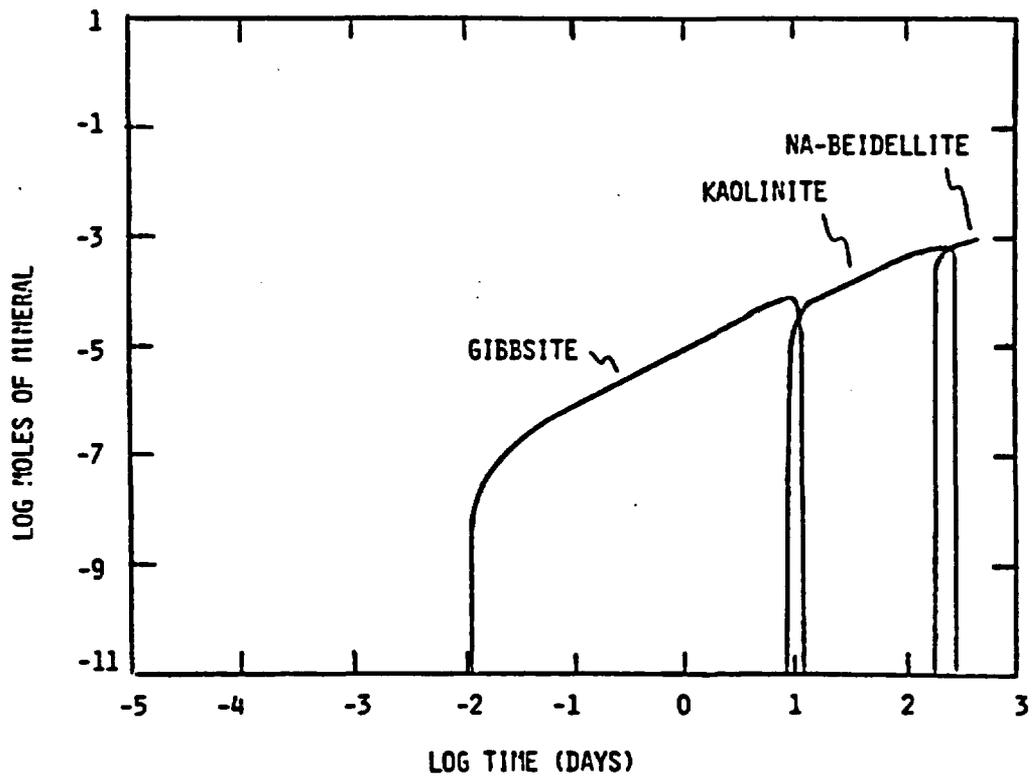


Figure 25. The affinities to precipitate of quartz, cristobalite, and paragonite as functions of time.

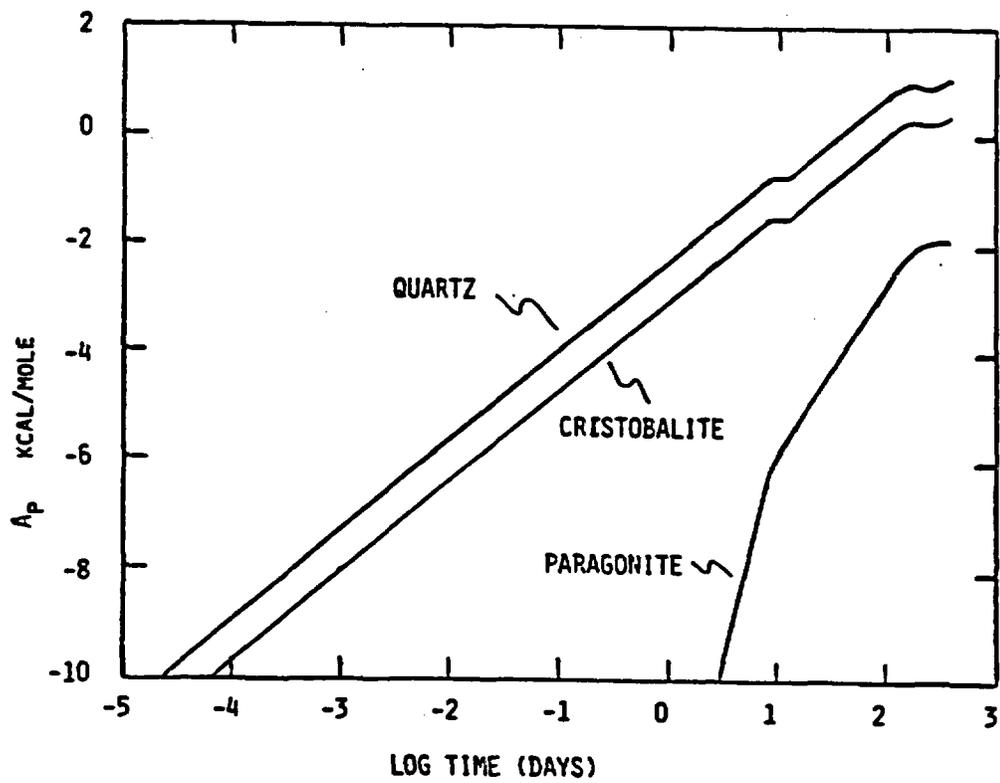
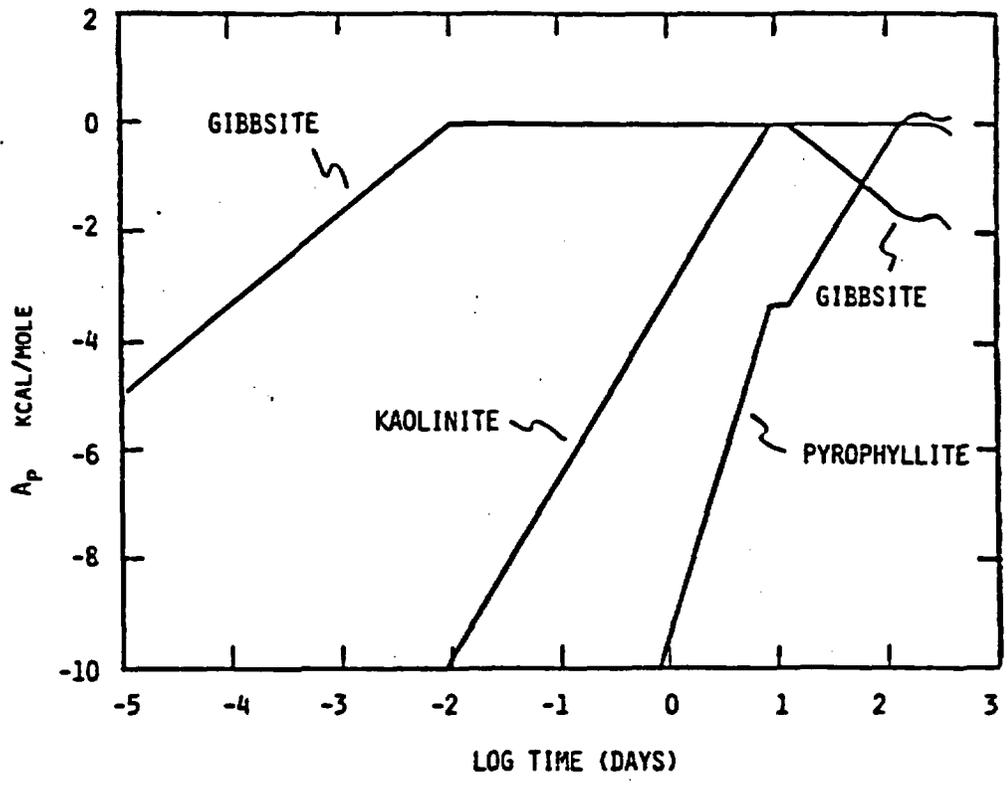


Figure 26. The affinities to precipitate of gibbsite, kaolinite, and pyrophyllite as functions of time.



in the system in equilibrium with the fluid phase are marked by where the corresponding affinity curves lie on the line of zero affinity. The fluid becomes supersaturated with pyrophyllite near the end of the run, and therefore it was necessary to suppress it to keep it from appearing in the calculated phase assemblage. However, the extent of supersaturation is quite small (128 calories at the end of the run, according to Figure 19(b)).

This calculation should give a fair to good prediction of experimental results. It would be fair, however, to point out some possible weaknesses. It is doubtful that gibbsite would precipitate from aqueous solution quite so rapidly early in the reaction (saturation occurs near 10^{-2} day). It is more likely that the solution would supersaturate with gibbsite, rising to some maximum value of A_p , then dropping back to zero according to precipitation growth kinetics. This sort of behavior has been observed in a tuff-water interactions experiment at 150°C (Knauss et al., 1983), which underscores the need to include some treatment of precipitation kinetics in these kinds of models. The next most serious weakness is that quartz, chalcedony, or cristobalite is likely to start growing at some point, although there is currently no way to predict this. A solid solution model for the montmorillonite would improve the results as well, obviating the need to suppress precipitation of pyrophyllite. However, it is possible that most of the possible improvement here could be made by simply putting one or more somewhat more aluminous Na-beidellite compositions into the data base.

7. THERMODYNAMIC CALCULATIONAL METHODS

7.1. INTRODUCTION

The governing equations and associated constraints were introduced in Chapter 3. This chapter and the following one continue the development begun there, to show how EQ6 actually solves those equations. From the standpoint of logical continuity, this chapter might have directly followed that one. However, there is a very fundamental reason for not doing so, namely that the material in Chapter 3 is essential to using EQ6, while the material here is not.

As was pointed out in Chapter 3, the governing equations and associated constraints are divided into two numerically separable types of problems (though these may still be linked in the fashion discussed earlier). The first problem deals with the equations that present themselves in the calculation of thermodynamic equilibrium. These equations are fundamentally algebraic (e.g., mass balance, mass action). The second problem deals with rate equations, which by nature ordinary differential equations (or ODEs, as they are often called). The calculational problem here is one of integration. Generally, this integration must be carried out numerically.

This chapter discusses the means by which EQ6 carries out thermodynamic equilibrium calculations. The reader familiar with how EQ3NR performs its thermodynamic calculations (Wolery, 1983, Chapter 8) will note that EQ6 uses essentially the same methodology. In fact, EQ3NR was created primarily from the earlier EQ3 (Wolery, 1978, 1979) by adapting the numerical methodology that had proven so successful in EQ6. The following chapter deals with the treatment of the rate equations, which is a unique function of EQ6 among the codes in the EQ3/6 package.

7.2. THE NEWTON-RAPHSON METHOD

The Newton-Raphson method is a very popular iterative technique for solving non-linear systems of algebraic equations. Discussion here of the general features of the method will be brief. The method is a topic in almost any introductory text on numerical methods (e.g., Carnahan et al., 1969) as well as almost any work dealing with the numerical methods used specifically to solve chemical equilibrium problems (e.g., Van Zeggeren and Storey, 1970).

The procedure for executing the method is fairly simple. 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 which has a value of zero when the n equations are satisfied. Both \underline{z} and $\underline{\alpha}$ are of length n .

Let k be the number of iterations, such that \underline{z}_k and α_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

$$\underline{J} \underline{\delta} = -\underline{\alpha} \quad (7-1)$$

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

$$\underline{J} = (\partial a_i / \partial z_j) \quad (7-2)$$

where i and j are the matrix coordinates. The correction term is then used to generate a new iteration variable vector by adding it to the old one:

$$\underline{z}_{k+1} = \underline{z}_k + \underline{\delta}_k \quad (7-3)$$

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 converged satisfactorily.

Two artistic aspects come into play at the start of using this method. First, the problem itself starts with, say, m equations and unknowns, and one usually tries to pare this number down to n less than m by a series of appropriate substitutions. The remaining n iteration variables are sometimes termed "master" variables. Second, given that one is going to deal with n equations in n unknowns, there is an infinite variety of ways to manipulate these equations to construct residual functions.

Neither of the above sorts of manipulations is unique to the Newton-Raphson method, but the choices made here can have a great impact on its success. The method tends to converge quickly if it does indeed converge. In its pure form, however, its behavior can be quite erratic in terms of whether or not it actually does converge. To make the method routinely successful in a given application, it is necessary to make wise choices in defining the residual functions and master iteration variables that are used, and follow this up by the use of appropriate convergence enhancement techniques (some of these are described below in Section 7.3).

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,

$$\delta_{i,k+1} = \sum_{j=1}^n p_{i,j} \delta_{j,k}^2 \quad (7-4)$$

where the $p_{i,j}$ are constants. This behavior suggests that in a 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 and EQ6) defined as

$$\delta_{\text{func},k+1} = 1 - (\delta_{\max,k+1}/\delta_{\max,k}) \quad (7-5)$$

therefore tends to approach (from below) a value of unity when convergence is rapid. Convergence to a significantly lesser apparent limiting value, say ≈ 0.72 instead of ≈ 0.99 , usually implies a minor error in the writing of the Jacobian matrix.

In EQ6, subroutine NEWTNZ carries out the Newton-Raphson iteration. Subroutine BETAZ computes the residual functions. Subroutine MATRXZ, with the assistance of a few subordinate routines, writes the Jacobian matrix.

7.3. METHODS TO AID CONVERGENCE

Several techniques are used in EQ6 to aid convergence of the thermodynamic equilibrium calculations. They include:

1. Use of logarithmic iteration variables
2. Under-relaxation techniques
3. Optimization of starting estimates
4. Basis-switching

These methods are also used in EQ3NR calculations (Wolery, 1983), so discussion here will be brief.

The physical quantities that correspond to the iteration variables that are used by EQ6 are all intrinsically positive (e.g., masses, ionic strength). Use of logarithmic iteration variables prevents the iteration from proceeding into non-physical ranges. Other than the fact that species masses rather than concentrations are used as master variables, the usage of this technique is the same as in EQ3NR.

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

$$z_{k+1} = z_k + \kappa \delta_k \quad (7-6)$$

where κ is a positive number less than one. There are several methods of applying under-relaxation. EQ6 uses two simple ones. These are identical to those used in EQ3NR (Wolery, 1983).

The first of these limits the size of the largest correction term:

$$\kappa = \delta' / \delta_{\max} \quad (7-7)$$

where δ' (SCREW5 in EQ6) 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 does diverge. This information may be used by EQ6 to pick a phase to delete from the phase assemblage (See Section 7.6) or to enter the redox scan mode (Section 7.7).

The other under-relaxation method incrementally reduces κ as necessary to reduce an absolute measure of divergence defined as $\beta_{\max,k+1} - \beta_{\max,k}$. This technique is not applied beyond the first several iterations. It is merely used to help keep the iteration from blowing up in the first few steps. In practice, this control comes into play relatively infrequently in EQ6 compared with the one described above.

Optimization of starting estimates is handled in a manner essentially the same as that in EQ3NR. If a normalized mass balance residual (an element of the β array) is excessively large or small, the corresponding log mass variable will be successively decremented or incremented until it is in a reasonable range. A general rule is that negative mass balance residuals should be avoided at the start of iteration. Experience with EQ6 has shown that negative mass balance residuals tend to get worse during iteration, with

divergence being more likely to occur the more negative the residuals are at the start. In contrast, no serious problem generally results when the mass balance residuals are high but positive, say for example high by 100%.

Basis switching, the practice of changing the aqueous species in the master set during execution of EQ3NR or EQ6, is often a very beneficial and sometimes also necessary device in order to achieve convergence. The general rule is that it is best to choose a master species that makes up a significant fraction of the corresponding mass balance. For example, if $\text{UO}_2(\text{CO}_3)_2^{2-}$ makes up most of the total UO_2^{2+} balance, then it, not UO_2^{2+} , is the better choice for the corresponding master species. Experience with the Newton-Raphson method in EQ3NR and EQ6 has shown that basis-switching is not especially critical to achieving convergence. It is not critical to use the most abundant species as the master species, but it is important that the master species not be an extremely scarce fraction.

Basis switching in EQ6 now simply follows any instructions on the INPUT file. Usually this means that EQ6 just follows any basis switching selections executed by EQ3NR. These in turn may have been user-specified (on the EQ3NR INPUT file) or chosen by EQ3NR itself (See Wolery, 1983). There has not thus far been any reason to incorporate any "smart" basis switching capability into EQ6, though it is conceivable that problems may be found which will require this.

7.4. ORGANIZATION OF THE ALGEBRAIC EQUATIONS AND ITERATION VARIABLES

In the EQ6 code, mass variables are used in place of concentration variables, as is the case in the EQ3NR code (Wolery, 1983). The number of equations and unknowns is reduced by substituting all governing aqueous mass action equations into the equations for mass and electrical balance and those equations which define ionic strength functions. The remaining aqueous species giving rise to unknown mass variables then comprise a relatively small master set. As a trade-off, the ionic strength (I) and the equivalent

stoichiometric ionic strength (I_E), where relevant, must be included as master iteration variables. As a whole, however, this approach considerably reduces the size of the Jacobian matrix.

Before proceeding, it is necessary to introduce some important notation. The letter ℓ will denote a logarithmic variable. It will be superscripted to denote the appropriate physical quantity:

1. a - thermodynamic activity
2. m - molal concentration
3. n - mass (in moles)
4. γ - molal activity coefficient
5. f - fugacity

The superscript will be omitted when the quantity in question is an ionic strength function, which is indicated by the subscript. Subscripts denote the specific species or parameters. The subscripts that are used in conjunction with the ℓ notation include:

1. s - any aqueous species
2. l ($s = 1$) or w - denotes solvent water
3. s_B - denotes the fictive aqueous species $O_2(g)$
4. s' - implies an aqueous master species other than $H_2O(l)$ or $O_2(g)$
5. s'' - implies a non-master aqueous species
6. I - ionic strength
7. I_E - equivalent stoichiometric ionic strength (Helgeson et al., 1970)
8. ϕ - a pure mineral
9. $\sigma\psi$ - the σ -th component of the ψ -th solid solution
10. g - a gas species

The usage of this notation is illustrated by the following examples:

$$\ell_s^m = \log m_s$$

(7-8a)

$$l_s^n = \log n_s \quad (7-8b)$$

$$l_1^a = \log a_w \quad (7-8c)$$

$$l_{s_B}^f = \log f_{O_2} \quad (7-8d)$$

$$l_{I_E} = \log I_E \quad (7-8e)$$

$$l_I = \log I \quad (7-8f)$$

$$l_s^Y = \log \gamma_s \quad (7-8g)$$

$$l_\varphi^n = \log n_\varphi \quad (7-8h)$$

$$l_{\sigma\psi}^n = \log n_{\sigma\psi} \quad (7-8i)$$

In this notation, the generalized mass action equation (3-4) can be written as

$$b_{ji} l_j^x + b_{1i} l_1^a + b_{s_B} l_{s_B}^f + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'i} (l_{s'}^m + l_{s'}^Y) \quad (7-9)$$

where the superscript "x" in the leading term is "f" for fugacity if the j-th species is a gas species, and "a" for activity in any other case. In EQ6, mass action is treated in terms of mass variables, instead of concentrations. Therefore, it becomes convenient to recast equation 7-9 into appropriate forms with this functional dependency. In order to derive these forms, the logarithmic variable in the leading term must be replaced by the appropriate forms given by equations 3-5a through 3-5d. It is also necessary to use the important logarithmic transformation of equation 3-1:

$$l_s^m = \log \omega + l_s^n - l_1^n \quad (7-10)$$

For an aqueous non-master species (denoted by s'' , whose corresponding destruction reaction is denoted by r), this yields (after some rearrangement) the important equation

$$\begin{aligned} \ell_{s''}^n = & (1/b_{s''r}) [\log K_r - b_{s''r} \ell_{s''}^Y - b_{1r} \ell_1^a - b_{s_B r} \ell_{s_B}^f \\ & - b_r^T (\log \omega - \ell_1^n) - \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'r} (\ell_{s'}^n + \ell_{s'}^Y)] \end{aligned} \quad (7-11)$$

where

$$b_r^T = b_{s''r} + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'r} \quad (7-12)$$

For the φ -th pure mineral, mass action can be written in the form

$$\log K_\varphi = b_{1\varphi} \ell_1^a + b_{s_B \varphi} \ell_{s_B}^f + b_\varphi^T (\log \omega - \ell_1^n) + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\varphi} (\ell_{s'}^n + \ell_{s'}^Y) \quad (7-13)$$

where

$$b_\varphi^T = \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\varphi} \quad (7-14)$$

Note that b_φ^T differs slightly in form from b_r^T : there is no $b_{\varphi\varphi}$ term analogous to $b_{s''r}$.

Similar forms can be written for components of solid solutions and for gas species ($b_{\sigma\psi}^T$ and b_g^T being defined analogously to b_ϕ^T , not to b_r^T). However, they will not be given here, as the preceding examples are sufficient to meet the immediate purpose, familiarizing the reader with the notation and with the concept of dealing with mass action equations in terms of mass variables.

In EQ6 the number of unknowns is reduced by eliminating the mass variables corresponding to the non-master aqueous species. This parallels what is done in EQ3NR, where the same thing is done with concentration variables. Equation 7-13 is substituted into the equations for mass and charge balance and the definitional relations for the ionic strength functions, in order to eliminate these parameters.

As in EQ3NR, there remain two major variants in the structure (as described by Wolery, 1984a), depending on the nature of the activity coefficient options. The first activity coefficient structure (ACS I) is the original structure (Wolery, 1978, 1979), and is used in cases where the activity coefficient functions (including the function that describes the activity of water) depend only on the ionic strength. This is slightly modified in the case of the B-dot option package (IOPG1 = 0), where the activity of water is calculated from the equivalent stoichiometric ionic strength of a sodium chloride solution (Helgson et al., 1970).

The second activity coefficient structure (ACS II) must be used when the activity coefficient functions depend on the specific composition of the aqueous solution (i.e., the ionic strength and the concentrations of the dissolved components). This structure is used for such options as the use of Pitzer's (1973, 1975) equations (IOPG1 = 1). The general key to which structure is used is: ACS I for IOPG1.LE.0, ACS II for IOPG1.GE.1.

The iteration variable array \underline{z} for EQ6 is defined by equation 7-15:

$\underline{z} =$

$$z_{s}^n, s = 1, s_B - 1$$

$$z_{s_B}^f$$

$$z_{s}^n, s = s_B + 1, s_Q$$

$$z_1^a$$

$$z_{s'}^Y, s' = 2, s_Q$$

$$z_{s''}^Y, s'' = s_Q + 1, s_T$$

$$z_{I_E}$$

$$z_I$$

$$z_{\varphi}^n, \varphi = 1, \varphi_E$$

$$z_{\sigma\psi}^n, \psi = 1, \psi_E, \sigma = 1, \sigma_{T,\psi}$$

1. Strict basis species:
masses of aqueous species
and fugacity of $O_2(g)$

2. Auxiliary basis aqueous
species - masses.

3. Activity of water and
molal activity coefficients
of all solute aqueous
species. (7-15)

4. Equivalent stoichiometric
ionic strength and true
ionic strength.

5. Pure minerals - masses.

6. Components of solid
solutions - masses.

Note that it may consist of six blocks. Not all of these may actually appear at a given point in a given model. The first block consists of logarithmic mass parameters for strict basis species, along with the logarithm of the oxygen fugacity. The second block consists of the same for auxiliary basis species that are treated as master variables (i.e., are treated as distinct components). The second block actually can not appear in the current version of EQ6, because this treatment is presently not permitted. It will be permitted when the redox disequilibrium option is effected.

The third block consists of logarithmic variables for the activity of water and the molal activity coefficients of the aqueous solute species. It appears only in ACS II. Note that the activity coefficient variables for non-master aqueous species appear in this block. The fourth block consists of the logarithmic ionic strength variables. When the equivalent stoichiometric ionic strength is not used, the corresponding logarithmic parameter still appears in the fourth block, but is treated as a "fixed" or "dead" variable.

The fifth block consists of the logarithmic masses of any pure minerals in equilibrium with the aqueous solution. The number of such is ϕ_E . The sixth block consists of the same for any solid solution components. Here ψ_E is the number of such solid solutions, and $\sigma_{T,\psi}$ is the number of components in the ψ -th solid solution.

This block structure is paralleled in the form for the residual function array ($\underline{\alpha}$), given by equation 7-16:

$\alpha =$

$$\alpha_{s}^n, s = 1, s_B - 1$$

$$\alpha_{s_B}^z$$

$$\alpha_{s}^n, s = s_B + 1, s_Q$$

$$\alpha_1^a$$

$$\alpha_{s'}^y, s' = 2, s_Q$$

$$\alpha_{s''}^y, s'' = s_Q + 1, s_T$$

$$\alpha_{I_E}$$

$$\alpha_I$$

$$\alpha_{\varphi}^n, \varphi = 1, \varphi_E$$

$$\alpha_{\sigma\psi}^n, \psi = 1, \psi_E, \sigma = 1, \sigma_{T,\psi}$$

1. Mass balance residuals for strict basis species (in moles) and charge balance residual (in equivalents).

2. Mass balance residuals for auxiliary basis species.

3. Definitional residuals for the activity of water and for the activity coefficients of all aqueous solute species

(7-16)

4. Definitional residuals for the ionic strength functions.

5. Mass action residuals for pure minerals in equilibrium with the water

6. Mass action residuals for components of solid solutions in equilibrium with the water.

7.5. THE RESIDUAL FUNCTIONS AND THE JACOBIAN MATRIX

This section presents the equations for the residual functions and the elements of the Jacobian matrix as they are defined in EQ6. The residual function equations define the elements in equation 7-16. The Jacobian elements are then obtained by partial differentiation according to equation 7-2.

Blocks 1 and 2. Mass balances and charge balance. The residual function has the form

$$\alpha_s^x = w_1 n_1 + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} w_{s'} n_{s'} + \sum_{r=1}^{r_T} w_{s''} n_{s''} + (1 - \delta_{ss_B}) \left[\sum_{\varphi=1}^{\varphi_E} w_{\varphi} n_{\varphi} + \sum_{\psi=1}^{\psi_E} \sum_{\sigma=1}^{\sigma_{T,\psi}} w_{\sigma\psi} n_{\sigma\psi} \right] \quad (7-17)$$

Here $x = n$ (mass balance) if $s \neq s_B$, otherwise $x = z$ (charge balance).

δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ otherwise).

The weighting factors for the charge balance case are

$$w_1 = 0 \quad (7-18a)$$

$$w_{s'} = z_{s'} \quad (7-18b)$$

$$w_{s''} = z_{s''} \quad (7-18c)$$

For the mass balance case, the weights are the stoichiometric equivalence factors

$$w_1 = u_{1s} \quad (7-19a)$$

$$w_{s'} = u_{s's} \quad (7-19b)$$

$$w_{s''} = u_{s''s} \quad (7-19c)$$

$$w_\varphi = u_{\varphi s} \quad (7-19d)$$

$$w_{\sigma\psi} = u_{\sigma\psi s} \quad (7-19e)$$

The following Jacobian elements are independent of activity coefficient options:

$$\partial \alpha_s^x / \partial \lambda_1^n = 2.303 (w_1 n_1 + \sum_{r=1}^{r_T} H_{sr}^n b_r^T) \quad (7-20)$$

where

$$H_{sr}^n = w_{s''} n_{s''} / b_{s''r} \quad (7-21)$$

$$\partial \alpha_s^x / \partial \lambda_{s'}^n = 2.303 (w_{s'} n_{s'} - \sum_{r=1}^{r_T} H_{sr}^n b_{s'r}^T) \quad (7-22)$$

$$\partial \alpha_s^x / \partial \lambda_{s_B}^f = 2.303 (- \sum_{r=1}^{r_T} H_{sr}^n b_{s_B r}^T) \quad (7-23)$$

($w_{s_B} = n_{s_B} = 0$, so the form is the same as the two preceding equations.)

$$\partial \alpha_s^n / \partial \lambda_\varphi^n = 2.303 w_\varphi n_\varphi \quad (7-24)$$

$$\partial \alpha_s^n / \partial \lambda_{\sigma\psi}^n = 2.303 w_{\sigma\psi} n_{\sigma\psi} \quad (7-25)$$

The B-dot option is a special case of activity coefficient structure I (ACS I). The Jacobian elements particular to this case are

$$\partial \alpha_s^x / \partial \lambda_{I_E} = -2.303 \Gamma_{II_E} \sum_{r=1}^{r_T} H_{sr}^n b_{1r} \quad (7-26)$$

$$\partial \alpha_s^x / \partial \lambda_I = -2.303 \sum_{r=1}^{r_T} H_{sr}^n (\Gamma_{s''I} b_{s''r} + L_r) \quad (7-27)$$

where

$$L_r = \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} \Gamma_{s'I} b_{s'r} \quad (7-28)$$

and

$$\Gamma_{II_E} = \partial \lambda_1^a / \partial \lambda_{I_E} \quad (7-29)$$

$$\Gamma_{sI} = \partial \lambda_s^y / \partial \lambda_I \quad (7-30)$$

For other options under ACS I, such as the Davies equation option

$$\partial \alpha_s^x / \partial \lambda_{I_E} = 0 \quad (7-31)$$

$$\partial \alpha_s^x / \partial \lambda_I = -2.303 \sum_{r=1}^{r_T} H_{sr}^n (\Gamma_{s''I} b_{s''r} + \Gamma_{II} b_{1r} + L_r) \quad (7-32)$$

Here

$$\Gamma_{II} = \partial \lambda_1^a / \partial \lambda_I \quad (7-33)$$

For the case of options in ACS II, such as using Pitzer's equations,

$$\partial \alpha_s^x / \partial \lambda_{I_E} = 0 \quad (7-34)$$

$$\partial \alpha_s^x / \partial \lambda_I = 0 \quad (7-35)$$

$$\partial \alpha_s^x / \partial \lambda_1^a = -2.303 \sum_{r=1}^{r_T} H_{sr}^n b_{1r} \quad (7-36)$$

$$\partial \alpha_s^x / \partial \lambda_{s'}^{\gamma} = -2.303 \sum_{r=1}^{r_T} H_{sr}^n b_{s'r} \quad (7-37)$$

$$\partial \alpha_s^x / \partial \lambda_{s''}^{\gamma} = -2.303 w_{s''} n_{s''} \quad (7-38)$$

Block 3. Activity of water and activity coefficients. This block appears only in ACS II. The residual functions are defined

$$\alpha_1^a = \log a_w^{\text{calc}} - \lambda_1^a \quad (7-39)$$

and

$$\alpha_s^{\gamma} = \log \gamma_s^{\text{calc}} - \lambda_s^{\gamma} \quad (7-40)$$

or, more generally,

$$\alpha_s^x = \log x_s^{\text{calc}} - \lambda_s^x \quad (7-41)$$

where $x = a$ if $s = 1$, otherwise $x = \gamma$. The Jacobian elements are

$$\partial \alpha_s^x / \partial \lambda_1^n = - \sum_{\substack{s'=2 \\ s'' \neq s_B}}^{s_Q} \Gamma_{ss'} - \sum_{r=1}^{r_T} \Gamma_{ss''} [1 - (b_r^T / b_{s''r})] \quad (7-42)$$

$$\partial \alpha_s^x / \partial \lambda_{s'}^n = \Gamma_{ss'} - \sum_{r=1}^{r_T} \Gamma_{ss''} (b_{s'r} / b_{s''r}) \quad (7-43)$$

$$\partial \alpha_s^x / \partial \lambda_{s_B}^f = - \sum_{r=1}^{r_T} \Gamma_{ss''} (b_{s_B r} / b_{s''r}) \quad (7-44)$$

($\Gamma_{ss_B} = 0$, so this equation has the same form as the one above it.)

$$\partial \alpha_s^x / \partial \lambda_I = \Gamma_{sI} \quad (7-45)$$

$$\partial \alpha_s^x / \partial \lambda_1^a = -\delta_{s1} + \Gamma_{sI} - \sum_{r=1}^{r_T} \Gamma_{ss''} (b_{1r} / b_{s''r}) \quad (7-46)$$

$$\partial \alpha_s^x / \partial \lambda_{s'}^Y = -\delta_{ss'} - \sum_{r=1}^{r_T} \Gamma_{ss''} (b_{s'r} / b_{s''r}) \quad (7-47)$$

$$\partial \alpha_s^x / \partial \lambda_{s''}^Y = -\delta_{ss'} - \Gamma_{ss''} \quad (7-48)$$

Here

$$\Gamma_{ss'} = \partial \alpha_s^x / \partial \lambda_{s'}^m \quad (7-49)$$

and

$$\Gamma_{ss''} = \partial \alpha_s^x / \partial \lambda_{s''}^m \quad (7-50)$$

Block 4. Equivalent stoichiometric ionic strength and the ionic strength. The residual functions have the form

$$\alpha_j = -\delta_{I_E j} I_E - \delta_{I j} I + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} w_{s'} m_{s'} + \sum_{r=1}^{r_T} w_{s''} m_{s''} \quad (7-51)$$

Here $j = I_E$ or I . Likewise, $\delta_{I_E j} = 1$ if $j = I_E$, otherwise,

$$\delta_{I_E j} = 0. \quad \delta_{I j} = 1 \text{ if } j = I, \text{ otherwise } \delta_{I j} = 0.$$

For the case $j = I_E$, $w_{s'} = u_{s_E s'}$, where s_E refers to Na^+ or Cl^- .

For $j = I$, $w_s = z_s^2/2$. Note that α_{I_E} and α_I are defined differently than in earlier versions of EQ6 (Wolery, 1978, 1979).

The Jacobian elements independent of activity coefficient structure are

$$\partial \alpha_j / \partial \ell_1^n = -2.303 \left[\sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} w_{s'} m_{s'} + \sum_{r=1}^{r_T} (w_{s''} m_{s''} - H_{jr}^m b_r^T) \right] \quad (7-52)$$

where

$$H_{jr}^m = w_{s''} m_{s''} / b_{s'' r} \quad (7-53)$$

$$\partial \alpha_j / \partial \ell_{s'}^n = 2.303 (w_{s'} m_{s'} - \sum_{r=1}^{r_T} H_{jr}^m b_{s' r}^T) \quad (7-54)$$

$$\partial \alpha_j / \partial \ell_{s_B}^f = 2.303 \left(- \sum_{r=1}^{r_T} H_{jr}^m b_{s_B r}^T \right) \quad (7-55)$$

($w_{s_B} = m_{s_B} = 0$, so $\partial \alpha_j / \partial \ell_{s_B}^f$ has the same form as $\partial \alpha_j / \partial \ell_{s'}^n$.)

Under the B-dot option,

$$\partial \alpha_j / \partial \lambda_{I_E} = -2.303 (\delta_{I_E j} I_E + \Gamma_{II_E} \sum_{r=1}^{r_T} H_{jr}^m b_{lr}) \quad (7-56)$$

$$\partial \alpha_j / \partial \lambda_I = -2.303 \left\{ \delta_{Ij} I + \sum_{r=1}^{r_T} [H_{jr}^m (\Gamma_{s''I} b_{s''r} + L_r)] \right\} \quad (7-57)$$

Under the general ACS I option, I_E is not used, and

$$\partial \alpha_I / \partial \lambda_{I_E} = 0 \quad (7-58)$$

$$\partial \alpha_I / \partial \lambda_I = -2.303 \left\{ I + \sum_{r=1}^{r_T} [H_{Ir}^m (b_{s''r} \Gamma_{s''I} + b_{lr} \Gamma_{II} + L_r)] \right\} \quad (7-59)$$

For the options in ACS II,

$$\partial \alpha_I / \partial \lambda_{I_E'} = 0 \quad (7-60)$$

$$\partial \alpha_I / \partial \lambda_I = -2.303 I \quad (7-61)$$

$$\partial \alpha_I / \partial \lambda_1^a = -2.303 \sum_{r=1}^{r_T} H_{Ir}^m b_{lr} \quad (7-62)$$

$$\partial \alpha_I / \partial \lambda_{s'}^Y = -2.303 \sum_{r=1}^{r_T} H_{Ir}^m b_{s'r} \quad (7-63)$$

$$\partial \alpha_I / \partial \lambda_{s''}^Y = -2.303 w_{s''} m_{s''} \quad (7-64)$$

Block 5. Mass action for pure minerals. The residual function is

$$\alpha_{\varphi} = -\log K_{\varphi} + b_{1\varphi} \lambda_1^a + b_{s_B\varphi} \lambda_{s_B}^f + b_{\varphi}^T (\log \omega - \lambda_1^n) + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\varphi} (\lambda_{s'}^n + \lambda_{s'}^Y) \quad (7-65)$$

$$\partial \alpha_{\varphi} / \partial \lambda_1^n = -b_{\varphi}^T \quad (7-66)$$

$$\partial \alpha_{\varphi} / \partial \lambda_{s'}^n = b_{s'\varphi} \quad (7-67)$$

$$\partial \alpha_{\varphi} / \partial \lambda_{s_B}^f = b_{s_B\varphi} \quad (7-68)$$

For the ACS I B-dot option,

$$\partial \alpha_{\varphi} / \partial \lambda_{I_E} = b_{1\varphi} \Gamma_{1I_E} \quad (7-69)$$

$$\partial \alpha_{\varphi} / \partial \lambda_I = \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\varphi} \Gamma_{s'I} \quad (7-70)$$

Under the other ACS I options,

$$\partial \alpha_{\varphi} / \partial \lambda_{I_E} = 0 \quad (7-71)$$

$$\partial \alpha_{\varphi} / \partial \lambda_I = b_{1\varphi} \Gamma_{1I} + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\varphi} \Gamma_{s'I} \quad (7-72)$$

For the ACS II options,

$$\partial \alpha_{\varphi} / \partial \ell_{I_E} = 0 \quad (7-73)$$

$$\partial \alpha_{\varphi} / \partial \ell_I = 0 \quad (7-74)$$

$$\partial \alpha_{\varphi} / \partial \ell_1^a = b_{1\varphi} \quad (7-75)$$

$$\partial \alpha_{\varphi} / \partial \ell_{s'}^Y = b_{s'\varphi} \quad (7-76)$$

Block 6. Mass action for components of solid solutions. Here σ denotes the component, ψ the solid solution. Components are presently restricted to end members, which correspond to pure minerals. The residual function is

$$\begin{aligned} \alpha_{\sigma\psi} = & -\log K_{\sigma\psi} + b_{1\sigma\psi} \ell_1^a + b_{s_B\sigma\psi} \ell_{s_B}^f \\ & + b_{\sigma\psi}^T (\log \omega - \ell_1^n) + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\sigma\psi} (\ell_{s'}^n + \ell_{s'}^Y) \\ & + b_{\sigma\psi\sigma\psi} (\log \chi_{\sigma\psi} + \log \lambda_{\sigma\psi}) \end{aligned} \quad (7-77)$$

where

$$b_{\sigma\psi}^T = \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\sigma\psi} \quad (7-78)$$

Here also x is the mole fraction of the component and λ is the corresponding activity coefficient. The mole fraction is given by

$$x_{\sigma\psi} = \frac{n_{\sigma\psi}}{\sum_{i=1}^{\sigma_{T,\psi}} n_i} \quad (7-79)$$

where $\sigma_{T\psi}$ = number of components in the ψ -th solid solution present in equilibrium with the water. Note that it follows that

$$\partial \log x_{\sigma\psi} / \partial \ell_{i\psi}^n = \delta_{\sigma i} - x_{i\psi} \quad (7-80)$$

The ACS-independent Jacobian elements are

$$\partial \alpha_{\sigma\psi} / \partial \ell_1^n = - b_{\sigma\psi}^T \quad (7-81)$$

$$\partial \alpha_{\sigma\psi} / \partial \ell_{s'}^n = b_{s'\sigma\psi} \quad (7-82)$$

$$\partial \alpha_{\sigma\psi} / \partial \ell_{s_B}^f = b_{s_B\sigma\psi} \quad (7-83)$$

$$\partial \alpha_{\sigma\psi} / \partial \ell_{\sigma\psi}^n = b_{\sigma\psi\sigma\psi} \left[(\Lambda_{\sigma\sigma\psi} + 1)(1 - x_{\sigma\psi}) - \sum_{\substack{j=1 \\ j \neq \sigma}}^{\sigma_{T,\psi}} \Lambda_{\sigma j\psi} x_{j\psi} \right] \quad (7-84)$$

$$\partial \alpha_{\sigma\psi} / \partial \ell_{j\psi}^n = b_{\sigma\psi\sigma\psi} \left[-x_{j\psi} + \Lambda_{\sigma j\psi} (1 - x_{j\psi}) - \sum_{\substack{i=1 \\ i \neq j}}^{\sigma_{T,\psi}} \Lambda_{\sigma i\psi} x_{i\psi} \right] \quad (7-85)$$

Here

$$\Lambda_{ij\psi} = \partial \log \lambda_{i\psi} / \partial \log x_{j\psi} \quad (7-86)$$

These parameters are specific to the solid solution thermodynamic models being employed. For examples, see Wolery (1979; where S is used in place of Λ in the notation).

Under the ACS I 8-dot option,

$$\partial \alpha_{\sigma\psi} / \partial \ell_{I_E} = b_{I\sigma\psi} \Gamma_{I I_E} \quad (7-87)$$

$$\partial \alpha_{\sigma\psi} / \partial \lambda_I = \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\sigma\psi} \Gamma_{s'I} \quad (7-88)$$

For other ACS I options,

$$\partial \alpha_{\sigma\psi} / \partial \lambda_{I_E} = 0 \quad (7-89)$$

$$\partial \alpha_{\sigma\psi} / \partial \lambda_I = b_{1\sigma\psi} \Gamma_{1I} + \sum_{\substack{s'=2 \\ s' \neq s_B}}^{s_Q} b_{s'\sigma\psi} \Gamma_{s'I} \quad (7-90)$$

For ACS II options,

$$\partial \alpha_{\sigma\psi} / \partial \lambda_{I_E} = 0 \quad (7-91)$$

$$\partial \alpha_{\sigma\psi} / \partial \lambda_I = 0 \quad (7-92)$$

$$\partial \alpha_{\sigma\psi} / \partial \lambda_I^a = b_{1\sigma\psi} \quad (7-93)$$

$$\partial \alpha_{\sigma\psi} / \partial \lambda_{s'}^Y = b_{s'\sigma\psi} \quad (7-94)$$

7.6. FINDING THE PHASES TO PRECIPITATE TO SATISFY HETEROGENEOUS EQUILIBRIUM

Each Newton-Raphson calculation requires that a phase assemblage be specified in advance. EQ6 finds the correct phase assemblage by making a sequence of such calculations, in which the phase assemblage is changed from calculation to calculation according to algorithms described by Wolery (1979). There has been essentially no change in the algorithms that carry out this function. Therefore, only a brief description will be given here.

If such a Newton-Raphson calculation converges, EQ6 searches for cases of supersaturation, the extent of which is measured by the precipitation affinity (A_p). Phases which are suppressed or whose affinity functions are less than a specified tolerance (TOLSST) are ignored. The code picks one supersaturated phase, adds it to the phase assemblage, and tries again. In principle, more than one such phase could be added at the same time, but it is not generally profitable to do so. The number of supersaturations may far exceed the number of new phases that actually need to be precipitated. This results because precipitation of a phase reduces not only its own affinity, but also the affinities of other phases that are composed of the same components.

EQ6 chooses the phase to be added as the one with the ^{largest ?} scaled precipitation affinity. The scaled affinity is calculated by dividing the standard affinity by a scaling factor:

$$A_{p,i,\text{scaled}} = A_{p,i} / b_{i,\text{scale}} \quad (7-95)$$

The scaling factor is arbitrarily defined as the sum of the absolute values of the reaction coefficients:

$$b_{i,\text{scale}} = \sum_{s=1}^{S_Q} |b_{s,i}| \quad (7-96)$$

Other definitions (i.e., the sum of the molecular weights of the species appearing in the reaction, the number of atoms appearing in the reaction) are possible and might work as well. The justification for scaling is that it improves the probability, as shown by experience, of choosing the right phases. About 80% or more of the choices are correct when there is a large number of supersaturations, say twenty or more, and the figure gets better when there are only a few. Scaling helps because it tends to remove a bias in the unscaled affinity that favors phases with large molecular formulas (Wolery, 1979).

EQ6 has a capacity to delete phases from the phase assemblage. This capability is necessary because the algorithm for adding phases is not 100% accurate. It is also needed in reaction path calculations, where a phase in equilibrium with the water may become exhausted. The so-called transient secondary minerals behave in this manner.

There are two pathways in EQ6 leading to deletion from the phase assemblage. One occurs when the matrix is singular at the start of the iteration, indicating that the phase assemblage being tried probably violates the so-called "apparent" or "mineralogic" phase rule (Wolery, 1979, 1983). In this case, EQ6 looks for linear dependence in the rows of the Jacobian that describe heterogeneous equilibria (e.g., mineral solubilities). If such dependence is found, the code calculates conditional affinities for the phases involved, scales them, and deletes the phase with the most negative scaled conditional affinity.

A "conditional" affinity is the affinity of a phase if the solution is assumed to be in equilibrium with the remaining members of a set or subset of phases. Conditional affinities can always be defined for linearly dependent sets. For example, if a solution is in equilibrium with cristobalite (a form of SiO_2), this is sufficient to fix the affinity of quartz, its polymorph. See Wolery (1979) for further discussion of this pathway.

In the second pathway, the iteration proceeds for one or more iterations before diverging. Divergence generally is due to one of the following

conditions: (a) a mineral should be deleted, (b) the starting value for the oxygen fugacity is too far off the mark, or (c) the system is so ill-poised that the oxygen fugacity can not be defined with acceptable precision. Experience with the code shows that the use of the convergence enhancement features described earlier limits the possibilities to one of the above. There is no theoretical guarantee to this, however.

EQ6 analyzes the situation to determine what action to take in response to divergence. It uses four independent algorithms to attempt to pick candidate phases for deletion. An object function (Δ_{nj}) is calculated for the n-th algorithm and the j-th phase in the assemblage. The candidate of the n-th algorithm is the phase with the most negative value of the object function for that algorithm. This value (denoted simply as Δ_n) must actually be negative, otherwise no candidate is produced. The overall pick for deletion, if any, is the candidate among the possible four with the most negative object function. EQ6 deletes this phase, unless it determines that the problem lies instead with the redox variable (see below) and takes other corrective action.

One of the four deletion algorithms referred to above is much more important than the other three. Recall that one of the under-relaxation controls (SCREW5) limits the magnitude of the Newton-Raphson correction terms. This causes the calculation to diverge more slowly than it would otherwise. If a mineral does not belong in the phase assemblage, the strongest indication of this, after an apparent phase rule violation, is that its logarithmic mass variable plunges downward. The corresponding correction term commonly approaches a value of -SCREW5 (the SCREW5 default is 2.0, so this value is usually -2.0) before the matrix becomes numerically singular and the iteration crashes. The object function for the first algorithm is

$$\Delta_{1,j} = \ell_{j,k}^n - \ell_{j,0}^n \quad (7-97)$$

where j denotes the phase being tested, k denotes the value of the logarithmic mass variable at the last iteration, and 0 the starting value.

The other three algorithms were programmed into EQ6 prior to the full development of the convergence enhancement techniques that are now in the code. No study has been made of their significance to the operation of the code in its present state. Casual observation suggests that their current role may be entirely vestigial. See Wolery (1979) for a description of these algorithms.

If the starting value of the oxygen fugacity variable is more than about five log units away from the correct value, experience has shown that convergence becomes unlikely. This divergence tends to show up most strongly in the correction term for the log oxygen fugacity variable. Commonly, this correction term is at or near either -SCREW5 the last couple of iterations, or +SCREW5. This condition indicates that a better value for the starting value of this variable is required. The code goes into the redox scan mode in an attempt to find a good starting value if the magnitude of the last correction term for the log oxygen fugacity variable is SCREW5. This condition overrides any choice for phase deletion.

If the correction terms for the log oxygen fugacity variable oscillate in sign with magnitudes of the order of SCREW5, the system is probably ill-poised. If the residual functions have small magnitudes at this point, ill-poising is almost a certainty. The problem then is that the oxygen fugacity is so sensitive to the masses of the components in the system that the addition or subtraction of even one molecule of $O_{2(aq)}$ per kilogram of solvent can change the oxygen fugacity by orders of magnitude (or the corresponding Eh by on the order of 100 millivolts). An ill-poised system causes trouble in the calculation because the machine word length, even at 64 bits, is not sufficient to deal with this situation.

There are two methods of trying to deal with this situation. One would be to accept the results of the iteration process if the residual functions are all close to zero, even if the correction terms are not. The code presently does not do this. The second way, which the code does employ, is to assume that the ill-poising is limited to a very narrow range of reaction progress (encountered at a so-called redox jump), and make several attempts to step

over it, using the redox scan feature to pick up the oxygen fugacity on the other side of the jump.

7.7. THE REDOX SCAN FEATURE

The redox scan feature is used to try to generate a starting value for the log oxygen fugacity variable that will lead to convergence. As noted above, the starting value normally must be within about five log units to get convergence. A redox scan is a sequence of Newton-Raphson calculations with increasing or decreasing starting values for this variable. It terminates when either convergence is achieved or the whole range of the stability of water at the specified temperature and pressure has been covered.

The scan limits are set by reference to the reaction



the mass action equation for which can be written as

$$\log f_{\text{O}_2} = \log K_{\text{Eh}} + 4 \log a_{\text{H}^+} - 2 \log a_{\text{w}} \quad (7-99)$$

The scan limits are calculated by assuming that $\log a_{\text{w}} = 0$ and that the corresponding limits on $\log a_{\text{H}^+}$ are 0 and $\log K_{\text{w}}$ (the equilibrium constant for the dissociation of water into H^+ and OH^-). Thus,

$$\log f_{\text{O}_2} \text{ (upper limit)} = \log K_{\text{Eh}} \quad (7-100)$$

$$\log f_{\text{O}_2} \text{ (lower limit)} = \log K_{\text{Eh}} + 4 \log K_{\text{w}} \quad (7-101)$$

At 25°C and 1.013 bar pressure, $\log K_{\text{w}}$ has a value very near to -14.0. Hence, the oxygen fugacity range under these conditions spans about 56 log units.

8. REACTION PATH CALCULATIONAL METHODS

8.1. Introduction

This chapter discusses the calculational methods that apply to reaction paths, exclusive of those used to make thermodynamic calculations. There are four basic topics to be covered here. The first is continuous representation of the algebraic master variables (the vector \underline{z}) with respect to reaction progress (ξ) by means of finite differences. This ties into the second topic, how EQ6 locates phase boundaries. Here a "phase boundary" is a point of reaction progress(ξ) at which a phase appears or disappears. The third topic is the integration of the rate equations, which leads into the final topic, the finite difference representation of rate functions and their usage in numerical integration.

In this chapter much use will be made of truncated Taylor's series. Such a series for a function $y(x)$ has the form

$$y(x) = y(x_1) + \sum_{n=1}^i (1/n!) (d^n y/dx)_1^n (x - x_1) \quad (8-1)$$

where x is any point, x_1 is a point at which the derivatives in the summation are evaluated, and i is the order of the series. Examples of such truncated Taylor's series are equation 3-33 (relative rates as a function of ξ) and equation 3-37 (temperature as a function of ξ or t). In these examples, the point x_1 corresponds to $\xi = 0$ or $t = 0$, and the user defines the values of the derivatives as part of the input to the problem.

It is not always feasible to specify or directly evaluate the necessary derivatives. If a calculation is proceeding along a sequence of points on the x axis, a finite difference equation can be used to make an equivalent prediction of the value of y at some new point, called x_0 , using the values

of y at the j most recent points. Here x_1 is the closest point, and x_j is the farthest. The order of the calculation, i , is $j - 1$. See Carnahan et al. (1969) or any other introductory numerical methods text for an extended introduction to finite differences.

Corresponding to the i derivatives of order 1 through i are i finite differences of order 1 through i (this is not a one-to-one correspondence, see below). These finite differences are defined by the following equations:

$$f_1^{(1)}[y] = \frac{(y_1 - y_2)}{(x_1 - x_2)} \quad (8-2)$$

$$f_1^{(n+1)}[y] = \frac{\{f_1^{(n)}[y] - f_2^{(n)}[y]\}}{(x_1 - x_{n+2})} \quad (8-3)$$

Here the superscript in parentheses denotes the order, the subscript denotes the point to which the differences correspond, and the symbol in the brackets denotes the function which is being differenced. Note one important element of recursion in equation 8-3: the finite differences of order greater than one at the most recent point (x_1) are calculated from the finite differences at the immediately preceding point (x_2).

It is possible to use the following equation to estimate y as a function of x from these finite differences:

$$y(x) = y(x_1) + (x - x_1) \sum_{n=1}^i f_1^{(n)}[y] \prod_{j=1}^n (x - x_j) \quad (8-4)$$

The integrated form of this equation gives rise to the so-called quadrature formulas used in the numerical solution of ordinary differential equations (See for example Carnahan et al., 1969).

The writer prefers to deal instead with the equivalent form of truncated Taylor's series, primarily because the differential and integral forms are simpler and more familiar. An array of finite differences (f) whose elements

increase in order from 1 to i can be converted into the equivalent array of derivatives (d) by the simple linear transformation:

$$\underline{d} = \underline{D} \underline{f} \quad (8-5)$$

where D is an upper triangular matrix (Wolery, 1979). To construct D, it is first convenient to define an array w of the same length as d and f, where each element is defined by

$$w_n = x_1 - x_{n+1} \quad (8-6)$$

The matrix D being upper triangular, all the diagonal elements are ones and all elements in the lower triangle are zero. The following recursions permit calculation of the off-diagonal elements above the diagonal. For the first row,

$$D_{1,n} = D_{1,n-1} w_n \quad (8-7)$$

where n goes from 2 to i. The remaining elements may be calculated from

$$D_{m,n} = D_{m,n-1} w_n + D_{m-1,n-1} \quad (8-8)$$

where m goes from 2 to i-2, and n goes from m+1 to i.

The error in a truncated Taylor's series is usually estimated as a function of the step size $\Delta x (= x - x_1)$ from the magnitude of the first neglected term. Such an error expression is used to derive an algorithm for bounding the step size so as to keep the estimated error within some predetermined limit. In many finite difference algorithms, therefore, an estimate is constructed of this extra term. In EQ6, however, the last term in the truncated series is used instead, which has the effect of using a more

conservative bound. Therefore, letting j be the order of the term used to estimate the error ($j = i$ in EQ6, $j = i + 1$ in the more traditional treatment):

$$\text{Error } [y] = (1/j!) (d^j y/dx^j) (\Delta x)^j \quad (8-9)$$

where Error $[y]$ is the error in y . Requiring Δx to satisfy the condition

$$|\text{Error } [y]| \leq \text{Tolerance } [y] \quad , \quad (8-10)$$

where Tolerance $[y]$ (See SCREW1 and SCREW3, Chapter 5) is the error tolerance on y , then leads to the limit on the step size

$$\Delta x \leq \left(\frac{j! \text{Tolerance } [y]}{|d^j y/dx^j|} \right)^{(1/j)} \quad (8-11)$$

The finite differences in EQ6 range up to order six. The order is initially zero, and must be reset to zero at points where the derivatives being represented are actually discontinuous functions. Discontinuities occur at phase boundaries for secondary phases in equilibrium with the aqueous solution, and at points where primary reactants become exhausted. Otherwise, the order progressively builds up to a maximum of six. The order itself is actually computed following the treatment of Gear (1971ab). In essence, equation 8-11 is used to test the possible orders to find the one that gives the largest step size consistent with the specified error tolerance.

8.2. Finite Difference Representation of Algebraic Master Variables

There are several objectives of applying finite difference representations of the algebraic master variables. Such representations permit forecasting or prediction of the values of these variables at a new point of reaction progress from knowledge of their values at immediately preceding points. One usage in EQ6 is to use these predicted values as starting estimates for the Newton-Raphson calculation at the new point. If the thermodynamic

calculational capability required the input of very good starting estimates, this usage would provide it. However, the capability now in EQ6 does not require the provision of such good estimates in order to achieve convergence.

The finite difference representations of algebraic master variables do have other uses, however. They can be used, for example, to predict the locations of phase boundaries, as will be discussed in the next section. They can also be used to predict maxima in the masses of secondary mineral components, which is useful in the fluid-centered flow-through mode for protecting such phases from redissolving in the water. Another useful trait is that, when the step size is constrained to keep these representations accurate, there results a better distribution of points of reaction progress at which thermodynamic calculations are made. That is, there is a denser clustering of such points where there is a greater degree of change in the state of the system, as expressed by relatively greater rates of change in the algebraic master variables with respect to reaction progress.

The basic idea is to represent the k-th algebraic master variable by a truncated Taylor's series, which in this case can be written

$$z_k(\xi) = z_k(\xi_1) + \sum_{n=1}^i (1/n!) (d^n z_k / d\xi^n)_1 (\Delta\xi)^n \quad (8-12)$$

where ξ is a point of reaction progress, ξ_1 is a nearby point (in practice, the most recent point at which a thermodynamic calculation has been made), i is the order of the truncated series, the derivatives pertain to point 1, and $\Delta\xi (= \xi_0 - \xi_1)$ is the step size. The derivatives are estimated from finite differences, using equations 8-2 and 8-3 to calculate the differences themselves, and equation 8-5 to convert these results to derivative form.

The first derivative of equation 8-12 is useful in locating maxima in mineral masses, a useful function in the fluid-centered flow-through mode. Recall that the maximum of a function on an interval is either at one of the

ends of the interval or at a point at which the derivative is zero.

Differentiation of 8-12 yields

$$dz_k(\xi)/d\xi = \sum_{n=1}^i [1/(n-1)!] (d^n z_k / \xi^n)_1 (\Delta\xi)^{n-1} \quad (8-13)$$

If mineral masses are removed from the "equilibrium" part of the system, a characteristic of the fluid-centered flow-through system, then either the derivatives must be rescaled or the order of the method must be dropped to zero. In the interests of efficiency, the former option is used in EQ6. Rescaling is necessary only because EQ6 uses logarithmic mass variables ($z = \log n$) instead of linear ones (n). Rescaling is accomplished by computing the corresponding derivatives of the linear mass variable, reducing the mass remaining in the equilibrium part of the system, and back transforming. Temporarily using m instead of n to represent order, because n must here be used to represent mass, the first transformation is given by

$$d^m n / d\xi^m = 2.303 \sum_{j=1}^m \binom{m-1}{j-1} n^{m-1} d^j z / d\xi^j \quad (8-14)$$

where m goes from 1 to i . Note the appearance of the binomial coefficient. The value of n at x_1 (n_1) can then be reduced (usually by some factor such as 99%). This drops the logarithmic mass value z correspondingly (by two log units in the case of the 99% factor). After n_1 and z_1 are assigned their new values, the rescaled logarithmic derivatives may be calculated from the following equations

$$dz/d\xi = \frac{dn/d\xi}{2.303 n_1} \quad (8-15)$$

$$d^m z / d\xi^m = \frac{1}{2.303 n_1} \left[d^m n / d\xi^m - 2.303 \sum_{j=1}^{m-1} \binom{m-1}{j-1} d^{m-j} n / d\xi^{m-j} d^j z / d\xi^j \right] \quad (8-16)$$

A question of considerable importance in terms of the cost of reaction path calculations is whether or not it is necessary to keep these finite difference functions generally accurate by means of a tight tolerance limit and equation 8-11. Other reaction path codes, for example PHREEQE (Parkhurst et al., 1980), do not even employ such functions. It has been pointed out above that these difference functions must be kept accurate in the case of the fluid-centered flow-through mode and any mode which involves real kinetics. In other cases, it is not an absolute requirement, hence the appearance of the so-called "economy" mode of calculation now permitted in some cases (See NMODL2, Chapter 5). The reason is that general accuracy is not required for the remaining purposes of these functions, phase boundary searches (see below).

When these finite difference functions are kept generally accurate, EQ6 functions very analogously to the two "souped-up" versions of the old PATHI program noted in Chapter 1, both of which followed the differential equations approach and integrated by means of the Gear (1971ab) variable step-size, variable order, predictor-corrector method. The EQ6 finite-difference functions for algebraic master variables are predictor functions equivalent to the Gear predictors, but EQ6 "corrects" these predictions by means of the Newton-Raphson calculation to satisfy the governing algebraic equations (e.g., mass balance, mass action). The Gear corrector functions correct the predicted values to satisfy the differential counterparts of these governing equations. Better results are obtained with the EQ6 approach, but the cost of a run is about the same. This cost tends to be significantly greater than that of running in "economy" mode.

8.3. Locating Phase Boundaries

Location of phase boundaries (where a mineral in equilibrium with the solution disappears, where such a mineral appears just following saturation) depends on accurate finite difference representation of the algebraic master variables. However, phase boundary location does not depend on the condition expressed by equation 8-12. EQ6 is written so that the code cuts the step

size if a phase boundary is overstepped. This go-back condition insures an accurate phase boundary location.

There are three possible outcomes of a step size cut. If the reaction progress variable still lies over the phase boundary, another cut may be made. A cut may fall on the phase boundary, within the specified tolerances. Or the cut will result in a Newton-Raphson calculation at a closer point before the phase boundary, giving a new ξ_1 , and thereby increasing the accuracy of the finite differences in the neighborhood of the boundary. This process must eventually locate the boundary.

8.4. Integrating Rate Equations

For purposes of integration, rate equations are expressed as truncated Taylor's series. The central equation for calculating irreversible mass transfer in EQ6, equation 3-6, requires the integration of the relative rate of the k-th irreversible reaction ($d\xi_k/d\xi$) from ξ_1 to ξ_0 . A parallel equation (3-32) requires the integration of the inverse rate ($dt/d\xi$) over the same limits in order to calculate the time increment.

Letting r_k denote the relative rate of the k-th irreversible reaction, we can write the truncated Taylor's series:

$$r_k(\xi) = r_k(\xi_1) + \sum_{n=1}^i (1/n!) (d^n r_k / d\xi^n)_1 (\Delta\xi)^n \quad (8-17)$$

The integrated form is

$$\Delta\xi_k = r_k(\xi_1) \Delta\xi + \sum_{n=1}^i \frac{1}{(n+1)!} (d^n r_k / d\xi^n) (\Delta\xi)^{n+1} \quad (8-18)$$

The rate law for relative rates (equation 3-33) is already in the form of a truncated Taylor's series. In this case, equation 8-18 yields an exact

result. In the case where actual rate laws are specified, relative rates are calculated using equation 3-29, and the truncated Taylor's series must be generated using finite differences, using equations 8-2 and 8-3. Here equation 8-18 does not yield an exact answer, and it is necessary to control the step size using equation 8-11 to control the error.

The inverse rate ($dt/d\xi$) is treated in the same manner as relative rates for which actual rate laws are specified. It is calculated from equation 3-31. Here letting r_t stand for the inverse rate, the truncated Taylor's series equation for this function is

$$r_t(\xi) = r_t(\xi_1) + \sum_{n=1}^i (1/n!) (d^n r_t / d\xi^n) (\Delta\xi)^n \quad (8-19)$$

The integrated form is

$$\Delta t = r_t(\xi_1) \Delta\xi + \sum_{n=1}^i \frac{1}{(n+1)!} (d^n r_t / d\xi^n) (\Delta\xi)^{n+1} \quad (8-20)$$

Equation 8-20, like 8-18, is not exact, and the step size control represented by equation 8-11 must be implemented to retain accuracy.

True kinetic modeling requires the actual integration of differential equations, and except for the case where the rates are defined as functions of only a time variable, this integration must be accomplished numerically. In EQ6, the finite difference functions described above act as predictor functions that are essentially equivalent to those in the Gear (1971ab) method. Unlike the case of algebraic master variables, any "correction" step must be made using real finite difference corrector functions.

The need for a corrector cycle for the rate functions must be determined after the Newton-Raphson iteration does the correcting for the algebraic master variables. The code then evaluates the rate laws at the new point of reaction progress (ξ_0), using as input the corrected algebraic variables, and compares the resulting values with the values that were predicted using

equations 8-17 and 8-19. If the corresponding rate values differ by more than a specified tolerance, some corrective action is initiated. This may be either a corrector cycle, in which the finite difference representations used in the integrations represented by 8-18 and 8-20 are improved, using the tentative calculated rate information at the new point, or a cut in the step size. At the present time, the only course of action in EQ6 is to cut the step size.

A simple i -th order corrector function can be generated by dropping the $i+1$ -th point and adding the 0-th. Resetting the indexing of the points so that ξ_0 now is called ξ_1 , etc., the finite differences may be recalculated using equations 8-2 and 8-3. The rates at the latest point are taken to be the provisional values that were calculated by evaluating the rate laws. The \underline{D} matrix must be recalculated and the new finite differences converted to derivative form by applying equation 8-5. This brings us back to the level of equations 8-17 and 8-19. However, the integrations must now be performed over nominally different limits (the same points of reaction progress, but what was called ξ_1 is now called ξ_2 , and what was ξ_0 is now ξ_1 . $\Delta\xi$ is now $\xi_1 - \xi_2$. The equivalent forms of equations 8-18 and 8-20 are

$$\Delta\xi_k = r_k(\xi_1) \Delta\xi + \sum_{n=1}^i \frac{1}{(n+1)!} (d^n r_k / d\xi^n) (-\Delta\xi)^{n+1} \quad (8-21)$$

and

$$\Delta t = r_t(\xi_1) \Delta\xi + \sum_{n=1}^i \frac{1}{(n+1)!} (d^n r_t / d\xi^n) (-\Delta\xi)^{n+1} \quad (8-20)$$

Correction of this kind is an iterative process, hence convergence becomes an issue. In terms of efficiency, a general rule of thumb is that the step size should be cut if two corrector cycles are not sufficient.

The simple corrector described above is based on simple back-substitution and should give first order convergence behavior. This is not satisfactory in

the case of so-called "stiff" ordinary differential equations (See for example Carnahan et al., 1969, or Gear, 1971ab). The practical definition of stiff equations is that they require a second-order method for corrector iteration (most such correctors are based on the Newton-Raphson method). See Gear (1971ab) for a discussion of corrector functions for stiff equations. It will probably become necessary at some point to incorporate such functions into EQ6.

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APPENDIX A

GLOSSARY OF MAJOR VARIABLES IN EQ6

This glossary covers the major variables in the EQ6 code, exclusive of those pertaining to the calculation of the activity of water and the activity coefficients of aqueous solute species (See Wolery, 1983, Appendix B). Variable names may be preceded by the corresponding algebraic symbols used in this report, if any. Many of these names coincide with those used in EQ3NR (Wolery, 1983). As in EQ3NR, 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 (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.
	AEH1, ..., AEH5	Coefficients for computing $\log K_{Eh}$ as a function of temperature.
	AFCNST	The factor $\frac{2.303 R}{1000}$.
A	AFF	Affinity of a fixed composition mineral to precipitate, kcal.
	AFFLCX	Affinity of a solid-solution phase to precipitate.
	AFFRCT	The affinity of an irreversible reaction.
	AFFTOT	The overall affinity of all irreversible reactions.
	AFFX	Affinity of an end-member component of a solid solution.
	AFTARG	The target affinity used to find a phase boundary at which a new phase enters the equilibrium system.

	AGS	Coefficients for computing $\log K_g$ as a function of temperature.
	AKG	A work array that holds a copy of AKM.
<u>D</u>	AKM	The matrix for converting finite differences of ascending order into derivative form.
A_t	ALK	Titration alkalinity.
<u>α</u>	ALPHA	Residual function vector.
2.303	AL10	$\ln 10$.
	AMN	Coefficients for computing $\log K_\phi$ as a function of temperature.
	APX	Solid-solution thermodynamics parameters.
	ARS	Coefficients for computing $\log K_r$ as a function of temperature.
	ATWT	Atomic weight of a chemical element.
<u>β</u>	BETA	Residual function vector, with normalized mass balance elements.
β_{\max}	BETAMX	Largest absolute value of any element of BETA.
	BETMX0	The value of BETAMX at the previous step of reaction progress.
	CDAC	The exponent of the activity of a species in a transition state theory rate law.
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_r^T	CDRST	Stoichiometric summation factor for aqueous redox and dissociation reactions.

$b_{s\phi}$	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 itself.
b_{ϕ}^T	CDRMT	Stoichiometric summation factor for mineral dissolution reactions.
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 itself.
b_g^T	CDRGT	Stoichiometric summation factor for gas dissolution reactions.
	CESRB	The number of moles of a chemical element per mole of a "special" reactant.
c_{es}	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.
$c_{e\phi}$	CEMN	Stoichiometric mass coefficient of a pure mineral; CEMN(NC,NM) is the number of moles of the NC-th chemical element in one mole of the NM-th pure mineral.
c_{eg}	CEGS	Stoichiometric mass coefficient of a gas species; CEGS(NC,NG) is the number of moles of the NC-th chemical element in one mole of the NG-th gas species.
m	CONC	Molal concentration of an aqueous species.
log m	CONCLG	Log of molal concentration.
	CPLIM	Limit on the number of computing units used before a run terminates itself (See Chapter 5).
$b_{\phi, scale}$	CSCALE	Affinity scaling factor for pure minerals.

	CSIGMA	Stoichiometric factor appearing in transition-state theory rate laws (See Chapter 5).
$\underline{\delta}$	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.
$\Delta \xi$	DELZI	Increment of reaction progress (ξ).
	DF1	Finite difference functions (f) for algebraic master variables.
	DF2	DF1 at the previous point of reaction progress.
	DIREAC	Derivatives (d) of the inverse rate with respect to reaction progress.
Δt	DLTIME	Increment of time (in seconds).
	DLZIDP	Dump interval for the fluid-centered flow-through open system mode of calculation (See Chapter 5).
	DLZMN	Lower limit on the size of a reaction progress increment.
	DLZMX1	Upper limit on the reaction progress increment when running at zero order.
	DLZMX2	Upper limit on the reaction progress increment when running at an order of one or greater.
	DRELRC	Derivatives (d) of the relative rates of irreversible reactions.
\underline{w}	DSUM	Sum vector of reaction progress increments defined by equation 8-6. with respect to reaction progress.
$\partial z_k / \partial \xi$	DXLG	Derivatives (d) of algebraic master variables with respect to reaction progress.
	DXLGN	Values of the first derivatives of the algebraic master variables with respect to ξ at a new point of reaction progress, as estimated from finite differences.
	DZPRNT	Print interval, linear in reaction progress.
	DZPRLG	Print interval, logarithmic in reaction progress.
	E	A work array used in solving matrix equations.
Eh	EH	Default theoretical redox potential, volts.

$\Delta(nz)$	ELECTR	Fixed electrical imbalance carried in the calculations.
F	FARAD	The Faraday constant, 23062.3 cal/equiv-volt.
	FCTRL	Factorial array; i.e., FCTRL(3)=3!.
	FK	Ratio of effective to total surface area of a reactant.
f_{O_2}	F02	Equilibrium oxygen fugacity of the aqueous phase.
	F02LG	Log of the equilibrium oxygen fugacity of the aqueous phase.
f	FUG	Fugacity of a gas species.
log f	FUGLG	Log fugacity of a gas species.
	GG	A work array that has the same dimensions as AA.
log γ	GLG	Log of activity coefficient of an aqueous species
	GTR	Composition of the theoretical mineral assemblage (pure minerals and solid solutions in equilibrium with the water plus pure minerals, solid solution, and "special" reactants); expressed as grams of element per kilogram of "rock."
s_E	IACION	Index of the aqueous species (Na^+ or Cl^-) that defines the equivalent stoichiometric ionic strength (I_E).
	:BASIS	Array that contains a record of basis-switching.
	IBETMX	Index of the master algebraic variable that defines BETAMX.
	IER	An error flag parameter; appears in the argument list of many subroutines.
	IEXR	The index of reactants that have exhausted on the current step of reaction progress.
	IEXRT	The number of reactants that have exhausted on the current step of reaction progress.
	IFILE	Device number for the file containing the second half of the INPUT file (normally = 60; see Chapter 5).
σ_T	IKT	Number of end-member components in a given solid solution.
	IKTMAX	Maximum allowed number of end-members in any solid solution.
	IMECH	The number of terms in a transition-state theory rate law.
	IMCH:MX	Maximum allowed number of terms in a transition-state theory rate law.
	INDEX	Array that contains the indices of the master iteration variables that appear for a given problem.

IODB1, Debugging print option switches (See Chapter 5).
etc.

IOPT1, Program option switches (See Chapter 5).
etc.

IOPG1, Activity coefficient option switches (See Chapter 5).
etc.

IOPR1, Print option switches (See Chapter 5).
etc.

IORD Array of the possible orders of the finite difference
calculations at a given point of reaction progress.

IR A work array used in solving matrix equations.

ISTACK A 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 that it does.

JCODE Flag denoting the species type of an irreversible reactant:
= 0 Mineral
= 1 Solid solution
= 2 "Special reactant"
= 3 Aqueous species
= 4 Gas species.

JCT The number of chemical elements in a problem.

JFLAG Switch array that determines whether an auxiliary basis
species is treated as a basis species (JFLAG = 0) or
a dependent species (JFLAG = 30). In the first case,
the auxiliary basis species has its own mass balance
in the model, and in the second, its mass balance is
folded in with that of the corresponding strict basis
species.

JGFLAG Status switch array for gas species:
= 0 means the gas appears in the current model;
= 2 means it is thermodynamically suppressed.

JKFLAG Status switch array for solid solution end-member components:
 = 0 means the component appears in the current model;
 = 2 means it is thermodynamically suppressed
 = 4 means it could not be found among the minerals of fixed composition.

JGFLAG Status switch array for gas species:
 = 0 means the gas appears in the current model;
 = 2 means it is thermodynamically suppressed.

JGT The number of non-suppressed gas species in memory.

JMFLAG Status switch array for minerals of fixed composition
 = 0 means the mineral appears in the current model;
 = 2 means it is thermodynamically suppressed.

JMT The number of non-suppressed pure minerals in memory.

JREAC Status flag for irreversible reactants:
 = 0 Set to react
 = -1 Saturated, but reaction continues
 = 1 Exhausted
 = 2 Saturated, and any remaining mass has been transferred to the equilibrium system.

JRST The number of non-suppressed aqueous reactions in memory.

JSFLAG Status switch array for aqueous species
 = 0 means the species appears in the current model;
 = 2 means it is thermodynamically suppressed
 = 3 means it does not appear in the current model.

JSOL Array whose values define chosen treatments of solid-solution thermodynamics.

JSORT The indices of the aqueous species, sorted in increasing order of mass.

JST The number of non-suppressed aqueous species in memory.

JSTACK A work array used in sorting aqueous species in increasing order of concentration.

JTEMP Flag for controlling temperature change along a reaction path (See Chapter 5).

JXFLAG Status switch array for solid solutions
 = 0 means the mineral appears in the current model;
 = 4 means it 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.

JXT The number of non-suppressed solid solutions in memory.

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.

KGM1 Position of the activity of water variable in the INDEX array.

KGMQ Position in the INDEX array of the last activity coefficient variable corresponding to an aqueous master species.

KGMQ1 KGMQ + 1.

KGMT Position in the INDEX array of the last activity coefficient variable corresponding to an aqueous species.

KHYDR Variable denoting the position of H^+ in the set of master iteration variables.

KMAX Maximum dimension of the Jacobian matrix.

KM1 Position of the first pure mineral variable in the INDEX array.

KMT Position of the last pure mineral variable in the INDEX array.

KORD The maximum possible order of the finite difference calculations for a given step of reaction progress.

KPRS Flag on the INPUT file denoting whether or not data for phases in the physically removed system are appended.

KSAT Number of supersaturated pure minerals, excluding those that are suppressed.

KSB Variable denoting the position of the hypothetical aqueous species $O_2(g)$ in the set of master iteration variables; $KSB = KCT + 1$.

KSPPMX Limit on the number of steps of reaction progress from the last print point; a print is forced if $KSTPPR.EQ.KSPPMX$.

KSQ The number of aqueous species in the set of master iteration variables.

KSTEP The number of reaction progress steps that have been made in a run.

KSTPMX The limit on the number of reaction progress steps for a given problem.

KSTPPR The number of steps since the last print point.

KXI Position of the first solid solution component variable in the INDEX array.

KXISTQ Variable denoting the position of equivalent stoichiometric ionic strength in the set of master iteration variables; $KXISTQ = KSQ + 1$.

KXI Variable denoting the position of ionic strength in the set of master iteration variables; $KXI = KSQ + 2$.

KXMOD Flag defining the type of alter/suppress option (See Chapter 5; 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.

KXSAT Number of supersaturated solid solutions, excluding those that are suppressed.

KXT Position of the last solid solution component variable in the INDEX array.

log λ LAMLG Log of the activity coefficient of a solid-solution end-member component.

LSCANH The lower limit of a redox scan (See equation 7-101).

LSCANO The upper limit of a redox scan (See equation 7-100).

$\log n_{\phi}$	LOMN	Logarithms of the masses of pure minerals (in moles).
$\log n_{\sigma\psi}$	LOMX	Logarithms of the masses of solid solution components (in moles).
$\log n_s$	LOSS	Logarithms of the masses of aqueous species (in moles).
	LOTX	Logarithms of the masses of solid solution phases (in moles).
	MIPM	Rate of precipitation of product minerals forming according to solubility equilibrium in the fluid-centered flow-through system (NMODL1 = 3), defined as $dn_i/d\xi$, where n_i is the mass of the i-th mineral component.
	MODR	Mass of destroyed reactant (in moles).
	MODRS	MODR at the previous point of reaction progress.
	MOFFG	Moles of gas species added to the system at the start of a run; part of the fixed fugacity option.
n_{ϕ}	MOMN	Masses of pure minerals (in moles).
	$n_{\sigma\psi}$	MOMX
	MORR	Mass of remaining reactant (in moles).
	MORRS	MORR at the previous point of reaction progress.
n_s	MOSS	Masses of aqueous species (in moles).
	MOTX	Masses of solid solution phases (in moles).
	MPRMN	Masses of pure minerals (in moles) in the physically removed system.
	MPRMNB	Array used to read in MPRMN values from the INPUT file.
	MPRMX	Masses of solid solution components (in moles) in the physically removed system.
	MPRMXB	Array used to read in MPRMX values from the INPUT file.
	MSORT	The molal masses of the aqueous species, sorted in order of increasing value.
n_e	MTE	Total mass of an element, in moles.
	MTEB	Total mass of an element (in moles), as specified on the INPUT file.
	MTEAQ	Total mass of an element (in moles) in aqueous solution.

	MTES	Total mass of an element (in moles) at the previous point of reaction progress.
	MWTGS	Molecular weight of a gas species.
	MWTMN	Molecular weight of a pure mineral.
	MWTRC	Molecular weight of a reactant.
	MWTSS	Molecular weight of an aqueous species.
	NART	The number of aqueous species reactants.
	NCARB	The index of C or the aqueous master species (usually HCO_3^- or CO_3^{2-}) that is formally associated with carbonate mass balance.
	NCHLOR	The index of Cl or the master aqueous species (usually Cl^-) that formally corresponds to Cl^- mass balance.
$\sigma_{T\phi}$	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.
	NCORR	The number of corrector cycles, including step size cuts, if any, to achieve desired accuracy in the integration of the rate functions.
ϵ_T	NCT	Total number of chemical elements.
	NCTMAX	Maximum allowed number of chemical elements.
	NDAC	The index of an aqueous species whose activity appears as a factor in a transition theory rate law.
	NDACT	The number of activity factors appearing in a term of a rate law based on transition state theory.
	NDATA2	Device number of the DATA2 file.
	NDATA3	Device number of the DATA3 file.
	NDCTMX	Maximum allowed number of species whose activities can appear in a transition-state theory rate law term.
	NEND	Array that stores the indices of fixed composition minerals that correspond to end-member components of solid solutions.
	NFFG	The number of gas species whose fugacities are to be fixed during a run.
	NGRT	The number of gas species reactants.
	NGT	Total number of gas species read from the data file.

NGTMAX Maximum allowed number of gas species.
NH2G The index of the gas species $H_2(g)$.
NHYDR The index of H or H^+ .
NINPUT Device number (60) of the INPUT file.
NINPTS Device number (61) of the copy of the INPUT file (INPTS)
created by stripping out comment lines.
NMODL1 Option switch defining the physical system for the
calculation (See Chapter 5).
NMODL2 Option switch for "economy" mode (See Chapter 5).
NMRT The number of pure mineral reactants.
NMT Total number of minerals of fixed composition read from the
data file.
NMTMAX Maximum allowed number of minerals of fixed composition.
NO2G The index of the gas species $O_2(g)$.
i NORD The order of the finite-differences.
NORDMX The maximum order of the finite-differences.
NOUTPT Device number of the OUTPUT file.
NPKUP Device number of the PICKUP file.
NPRMN The number of pure minerals in the physically removed system
(as read from the INPUT file).
NPRMX The number of solid solutions in the physically removed
system (as read from the INPUT file).
NPRSMX Maximum allowed number of species in the physically removed
system that can be read from the INPUT file.
NRCT Total number of reactants (irreversible reactions).
NRCTMX Maximum allowed number of reactants (irreversible
reactions).
NRK Rate law code for irreversible reactions (See Chapter 5).
NRNDEX Array containing the regular species indices of
reactants associated with irreversible reactions.
NRSQ Number of reactions associated with auxiliary master
species; same as the number of auxiliary aqueous master
species.

r _T	NRST	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.
	NSB1	NSB + 1.
	NSK	Reactant surface area option switch: = 0 Constant surface area = 1 Constant specific surface area.
	NSODIU	The index of Na or the aqueous master species (usually Na ⁺) that formally corresponds to Na ⁺ mass balance.
s _Q	NSQ	Total number of aqueous master species.
	NSQMAX	Maximum allowed number of aqueous master species.
	NSQ1	Argument in a stoichiometric reaction coefficient array (CDRS, CDRM, BDRG) denoting the formally associated species (aqueous, mineral, or gas) that is destroyed in a given reaction; NSQ1 = NSQ + 1.
	NSRT	Number of special reactants on the INPUT file.
	NSRTMX	Maximum allowed number of special reactants.
s _T	NST	Total number of aqueous species read from the data file; includes all master species but other species only as needed for a given input problem.
	NSTMX	Maximum allowed number of aqueous species.
	NXMDMX	The maximum allowed value of NXMOD.
	NXMOD	The number of species/reactions affected by alter/suppress options (See KXMOD); read from the INPUT file.
	NXOPEX	The number of specified exceptions to the mineral subset-selection options for suppressing minerals.
	NXOPMX	The maximum allowed value of NXOPT.
	NXOPT	Total number of subset-selection options to suppress minerals. NXOPT appears on the INPUT file.
	NXPEMX	The maximum allowed value of NXOPEX.
	NXPG	The data file indices of gas species loaded from the data file DATA2; used in reading DATA3.

	NXPM	The data file indices of pure minerals loaded from the data file DATA2; used in reading DATA3.
	NXPS	The data file indices of aqueous species loaded from the data file DATA2; used in reading DATA3.
	NXRIDX	Index array for solid solution reactants [NXR = NXRIDX(NRC) is the solid solution reactant index that corresponds to the NRC-th reactant.].
	NXRT	The number of solid solution reactants.
	NXRMAX	The maximum allowed number of solid solution reactants.
ψ_T	NXT	Total number of solid solution phases read into memory
	NXTMAX	Maximum allowed number of solid solutions.
ω	OM	Water constant, $1000 \div$ the molecular weight of H_2O ; $\omega = 55.51$.
$\log \omega$	OMLG	Log of the water constant.
ϕ	OSCOFF	Osmotic coefficient of water.
	OXFAC	Stoichiometric equivalence factors for oxides.
	OXIDE	Composition of the mineral assemblage in equilibrium with the aqueous solution, expressed in terms of oxide components.
pe^-	PE	Log of activity of the hypothetical electron species.
P	PRESS	Pressure, bars.
	QBASSW	Logical switch; = .TRUE. if basis switching has taken place.
	QCORR	Logical switch; = .TRUE. if the corrector tolerance is satisfied.
	QDUMP	Logical switch used in connection with NMODL1 = 3; = .TRUE. flags a call to subroutine SHIFT to transfer secondary mineral mass out of the system.
	QFCP2	Logical switch; = .TRUE. when the assumed phase assemblage in the "equilibrium" system violates the apparent phase rule.
	QFLAG	Logical switch; = .TRUE. indicates that the temperature has just crossed $100^\circ C$.

QFLAG1 Logical switch; = .TRUE. indicates that the new temperature and the last temperature for which the thermodynamic data were recalculated lie on opposite sides of 100°C.

QMOD Logical switch; = .TRUE. indicates a change in the equilibrium phase assemblage.

QNOCHB Logical switch; = .TRUE. indicates that the charge balance equation is inactive.

QNUCOR Logical switch; = .TRUE. indicates that corrector cycles are not to be done even if the corrector tolerance is not satisfied (QNUCOR = QQMODE.OR.QSMODE.OR.QPMODE).

QNO CUT Logical switch; = .TRUE. indicates that step size cuts are not to be done to satisfy the corrector tolerance (QNO CUT=QSMODE.OR.QPMODE).

QPHASL Logical switch; = .TRUE. indicates that subroutine NEWTNZ is sliding forward in reaction progress to avoid numerical instability associated with a phase coming into or leaving the equilibrium phase assemblage.

QPMODE Logical switch; = .TRUE. indicates that QPHASL has been set to .TRUE. during the current call to subroutine NEWTNZ.

QPRINT Logical switch; = .TRUE. indicates that a print of the state of the system is to be made at the current point of reaction progress.

QQMODE Logical switch; = .TRUE. indicates that Newton-Raphson iteration has failed and can not be made to work at the current point of reaction progress.

QRIINF Logical variable; = .TRUE. indicates that the time has reached infinity.

QSMODE Logical switch; = .TRUE. indicates that subroutine NEWTNZ is in redox scan mode.

QTIME Logical switch; = .TRUE. indicates that the limit on the number of computing units has been exceeded.

R RCONST The gas constant, 1.98726 cal/mol-°K.

RES A work array used in solving matrix equations.

RIF1 Finite difference array (f) for the inverse rate.

RIF2 RIF1 at the previous point of reaction progress.

dt/dξ	RIREAC	The inverse rate.
	RIRECP	The predicted value of the inverse rate at a new point of reaction progress.
$\frac{-\alpha}{k}$	RHS	A negative copy of the array ALPHA.
	RK1, RK2, RK3	Rate constants (See Chapter 5).
dξ _i /dt	RREAC	The actual rate of an irreversible reaction.
dξ _i /du	RRELRC	The relative rate of an irreversible reaction.
	RRELRP	Predicted values of the relative rates of irreversible reactions at a new point of reaction progress.
	RRF1	Finite difference array (<u>f</u>) for relative rates.
	RRF2	RRF1 at the previous point of reaction progress.
	RXBAR	The mole fraction of a component in a solid solution reactant.
	RXBARB	The mole fraction of a component in a solid solution reactant (as read from the INPUT file).
	SCMAX	Array of step size scaling factors corresponding to different possible orders.
	SCREW1	Step size control parameter that bounds the magnitude of the highest order term in a truncated Taylor's series for a master algebraic variable.
	SCREW2	Step size cut parameter. If BETAMX exceeds this parameter at the start of Newton-Raphson iteration, EQ6 may cut the step size.
	SCREW3	Step size control parameter similar to SCREW1, but which bounds the highest order term in a truncated Taylor's series for a rate function.
	SCREW4	Tolerance on the difference between predicted and calculated rate functions. If exceeded, causes either a cut in the step size or a corrector cycle.
δl	SCREW5	Under-relaxation parameter that bounds the magnitude of a Newton-Raphson correction term.
s	SK	Surface area of a reactant.
	SSK	Specific surface area of a reactant.
S	SX	Solid solution derivative function.

u	STORE	Stoichiometric mass balance factor.
H	STOR1	The H factors defined in Chapter 7.
L _r	STOR2	The L _r factor defined Chapter 7.
	TCNST1	The number of seconds per day (86,400).
	TCNST2	The number of days per year (365.25).
	TDAYS	Model time (in days) at the latest point of reaction progress.
	TEMPC	Temperature °C.
	TEMPCI	The temperature (°C) at the end of the initializing EQ3NR or EQ6 run.
	TEMPCO	The temperature (°C) at $\xi = 0$ or $t = 0$.
T	TEMPK	Temperature °K.
t	TIME	Model time (in seconds) at the latest point of reaction progress.
	TIMEMX	Limit on the progress of model time (in seconds) specified on the INPUT file.
	TIMES	The value of time at the previous point of reaction progress.
τ	TITR	Titration factor of an aqueous species; the number of equivalents of alkalinity per mole of the species.
	TK1, TK2, TK3	First, second, and third order derivatives of temperature with respect to ξ or t .
	TLOGS	Logarithm of model time (seconds).
	TLOGD	Logarithm of model time (days).
	TLOGYR	Logarithm of model time (years).
	TOLAFT	The tolerance about the target affinity (AFTARG), used in predicting the location of a phase boundary at which a new phase enters the equilibrium system.
	TOLBT	Convergence bound on BETAMX.
	TOLDL	Convergence bound on DELMAX.
	TOLSAT	Supersaturation tolerance which the precipitation affinity must exceed before EQ6 will attempt to precipitate a phase.

TOLSST Supersaturation step size cut parameter. The step size is cut when the precipitation affinity of a phase exceeds this limit.

TOLX Tolerance for SERCH routines.

TOLXAT Covergence tolerance used by subroutine HPSATZ to compute the affinity function for a solid solution that is a potential precipitate (one not currently present in the equilibrium phase assemblage).

TSTRT Model time (in seconds) at the start of a problem.

TYEARS Model time (in years) at the latest point of reaction progress.

TZERO The temperature ($^{\circ}\text{C}$) for which the thermodynamic data were last calculated.

UACION The name of the aqueous species (Na^{+} or Cl^{-}) that defines the equivalent stoichiometric ionic strength (I_{E}).

UOAC The name of an aqueous species whose activity appears as a factor in a transition state theory rate law.

UELEM Name of a chemical element (its chemical symbol).

UELEMB Name of a chemical element on the INPUT file.

UENDB Name of a component of a solid solution reactant.

UEQLRN Alphanumeric string containing the release number of the supporting EQLIB library.

UEQLST Alphanumeric string containing the stage number of the supporting EQLIB library.

UESRB The name of a chemical element that makes up a "special" reactant.

UFFG The name of a gas species whose fugacity is to be fixed.

UGAS Name of a gas species (usually its chemical formula).

ULG1 Array containing the names of the master iteration variables.

UMIN Name of a mineral (usually its alphabetic name; more rarely, its chemical formula).

UNDMS Name of a data file master species, used to define a problem on the INPUT file.

UNRMS Name of a run master species to be used in running a problem. UNRMS and UNDMS pairs are specified together on the INPUT file. A basis switch is specified by the condition UNRMS.NE.UNDMS.

UOXIDE Name of an oxide.

UPRMN Name array for pure mineral in the physically removed system (read from the INPUT file).

UPRMX Name array for solid solution end members in the physically removed system (read from the INPUT file).

UREAC Name of a reactant associated with an irreversible reaction.

URELNO Alphanumeric string containing the release number of EQ6.

USOLX Name of a solid solution (its alphabetic name).

USPEC Name of an aqueous species (usually its chemical formula).

USTAGE Alphanumeric string containing the stage number of EQ6.

UTITL1 Main title (text), appearing on the first part of the INPUT file.

UTITL2 Title (text) from the lower part of the INPUT file; UTITL2. is the main title of the previous run.

UTITLD Title from the thermodynamic data file.

UXCAT Name of a component specified in connection with a subset-selection suppression option for solid phases (See Chapter 5).

UXMOD The name of a species affected by an alter/suppress option (See Chapter 5).

UXOPT An alphabetic string ("ALL" or "ALWITH") defining a subset-selection suppression option for solid phases (See Chapter 5).

UXTYPE An alphabetic string that describes a solid solution thermodynamics treatment.

VMINO The molar volumes of pure minerals at 25°C and 1.013 bar pressure.

VOLG The volume of a perfect gas at 298.15⁰K and 1 bar pressure, 22413.6 cm³.

VOLMN The volumes of pure minerals present in the equilibrium phase assemblage.

	VOLXX	The volumes of solid solutions present in the equilibrium phase assemblage.
	VREAC	The molar volume of a reactant.
W	W	Solid solution excess Gibbs energy parameter.
w	WEIGHT	Weighting parameters (see Chapter 7).
x	XBAR	Mole fraction of a solid-solution end-member.
log x	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.
I	XI	Ionic strength.
	XIC	Calculated ionic strength.
	XILG	Log of the ionic strength.
I _E	XISTEQ	Equivalent stoichiometric ionic strength.
	XISTLG	Log of equivalent stoichiometric ionic strength.
	XISTQC	Calculated equivalent stoichiometric ionic strength.
log K _{Eh}	XLKEH	Log of equilibrium constant of the half-reaction relating the hypothetical electron and O ₂ (g).
	XLKFFG	The logarithm of a desired fixed fugacity value.
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.
	ZKLOGL	Amount by which the log mass of a phase in the equilibrium system is decremented by a transfer to the physically removed system.
	ZKLOGU	Threshold/target value for the mass of non-aqueous phases (See Chapter 5 for a discussion of its usage).
ξ	ZI1	The value of reaction progress at the latest point.
	ZI2	The value of reaction progress at the previous point.

	ZIDUMP	The next point of reaction progress where a dump of minerals in equilibrium with the aqueous solution to the physically removed system is required by the dump interval parameter (DLZIDP); this is relevant only to the fluid-centered flow-through open system mode of EQ6.
	ZIMAX	The maximum limit on reaction progress (ZII, ξ), as defined on the INPUT file.
	ZIPR1	The next point of reaction progress where the linear print interval parameter (DZPRNT) requires a print.
	ZIPR2	The next point of reaction progress where the logarithmic print interval parameter (DZPRLG) requires a print.
ξ_i	ZIRCT	The reaction progress variable for an individual irreversible reaction.
	ZIRCTS	ZIRCT at the previous point of reaction progress.
	ZISTR	The value of reaction progress (ZI, ξ) at the start of a problem.
z	ZLG1	Array of master iteration variables.
$z_s^2/2$	ZSQ2	Array containing the squares of the electrical charges of the aqueous species, divided by two.

APPENDIX B

GLOSSARY OF EQ6 SUBROUTINES

EQ6 is a large code. "MAIN." refers to the main program. EQ6 also uses many of the routines from the EQLIB library (See Wolery, 1983, Appendix C).

- MAIN. Sets up the run. It connects the necessary files (INPUT, DATA2, DATA3, OUTPUT, and PICKUP). It initializes key arrays and sets default values for important run parameters. It also does some "idiot-proofing" checks on the input parameters.
- PATH Supervises the execution of a reaction path run.
- NEWTNZ Performs a thermodynamic equilibrium calculation, using the Newton-Raphson method. As part of this function, it determines which phases to add or drop from the phase assemblage. MAIN makes the first call to NEWTNZ for a given problem. PATH makes all subsequent calls.
- MATRXZ Writes the Jacobian matrix (AA, \underline{J}) for Newton-Raphson iteration.
- BETAZ Computes the Newton-Raphson residual functions (including ALPHA, $\underline{\alpha}$; BETA, $\underline{\beta}$; and BETAMX, β_{\max}).
- READZ Reads the INPUT file. It writes an "instant echo" of the INPUT data on the OUTPUT file (primarily to aid in debugging possible format errors on the INPUT file). READZ contains full internal documentation concerning the INPUT file.

- INDATZ Reads the thermodynamic data files DATA2 and DATA3 and calculates the values of temperature dependent parameters. REDATZ is an alternate entry for recalculating temperature dependent parameters after a change in temperature during a reaction progress run.
- ECHOZ Writes an echo of the INPUT data on OUTPUT. Unlike the "instant echo" written by READZ, this echo is intended to be kept as part of a permanent record of the run. It includes some data file statistics, any default values that were chosen by the code, and any changes in the INPUT constraint options made by the code to resolve inconsistencies.
- SCRIPZ Writes a detailed description of the state of the system at a point of reaction progress. The scope of these prints can be managed by the use of the IOPR print option switches.
- JGIBBS Determines which phase in a set should be dropped on an apparent phase rule violation.
- HPSATZ Computes the affinity function for a solid solution phase (AFFLCX) in the case where the phase is not part of the phase assemblage.
- SHIFT Shifts masses of non-aqueous phases from the "equilibrium" part of the system to the so-called "physically removed" system. This routine separates secondary phases from the moving packet of water in the flow-through open system model (NMODL1 = 3). It is also used to get rid of secondary phases at the start of a run, if desired (See IOPT5, Chapter 5).
- RESCAL Rescales the derivative functions of the logarithmic masses of secondary phases or components of secondary phases. Rescaling is necessary after a call to SHIFT, unless the order of the Taylor's series is zero.

GLXRN Decodes the names of reactants read from the INPUT file by determining the corresponding species indices. "Special" reactants have no such indices.

INNDX Decodes the names of master variable species read from the INPUT file by determining the corresponding species indices.

BSWCH Oversees any basis switching.

RSETUP Sets up the molecular weights and molar volumes of reactants.

ECHOLK Prints the names of species, their indices, and, if any, the equilibrium constants of the corresponding reactions.

SWTCH Executes basis switching between a pair of aqueous species; called by BSWCH.

COMP1 Calculates the values of many secondary parameters for subsequent output by SCRIPZ.

TSTEP Calculates the temperature and initiates recalculation of temperature dependent data, if necessary, by calling REDATZ (an alternate entry to INDATZ).

SATCHK Calculates the affinities to precipitate (A_p) of possible secondary phases and tests the saturation state of each.

MODEXZ Modifies the indexing of the Jacobian matrix, as when a new secondary mineral appears in the phase assemblage.

BALCAZ Computes the Jacobian matrix rows for the activity of water and the activity coefficients; called by MATRXZ.

BALCMZ Computes the Jacobian matrix rows for pure mineral mass action; called by MATRXZ.

BALCNZ Computes the Jacobian matrix rows for mass and charge balance; called by MATRXZ.

BALCSZ Computes the Jacobian matrix rows for solid solution component mass action; called by MATRXZ.

BALCXZ Computes the Jacobian matrix rows for the ionic strength and the equivalent stoichiometric ionic strength; called by MATRXZ.

FIND Fits the input points of a function to a smooth curve and returns the value fo the function at zero. FIND is called by the SERCH routines.

WTERM Computes the W(I,NX) coefficients for the excess free energy functions of solid solutions from the APX data read from the DATA3 file and the absolute temperature (TEMPK).

LAMDAZ Computes the activity coefficients (λ) of solid solution components.

SXTERM Computes the derivative functions of the activity coefficients of solid solution components.

DERSPC Computes the masses of non-master aqueous species. It also calculates the equilibrium fugacities of the relevant gas species. DERPSC is called by NCMPZ.

AFFUNC Calculates the affinity to precipitate (A_p) for pure minerals.

NCMPZ Computes all the parameters (masses, concentrations, etc.) needed to write the Jacobian matrix from the ZLGI array. NCMPZ is called by DERSPC.

TAYLOR Predicts the values of master variables from finite-difference based truncated Taylor's series.

- TAYLR2 Predicts the values of the first derivatives of master variables with respect to reaction progress from finite-difference based truncated Taylor's series.
- AKMATR Computes the AKM (D) matrix, which relates finite differences of ascending order to the corresponding derivatives. AKMATR is called by DERIV.
- DERIV Calculates estimates of the derivatives of master variables with respect to reaction progress from finite differences. DERIV evaluates the equation $(DXLG) = (AKM)(F1)$ [a form of equation 8-5], where DXLG is the array of derivatives, AKM is the matrix calculated by AKMATR, and F1 is the array of finite differences.
- LINDEP Tests the first JDIM elements of the first IDIM rows of the matrix AA for linear dependence. If such dependence is found, QFCP2 is returned with a value of .TRUE.
- PREAC Prints a chemical reaction.
- RTAYLR Evaluates finite-difference based truncated Taylor's series for the rates of all irreversible reactions ($d\xi_i/d\xi$, the relative rate, or $d\xi_i/dt$, the actual rate) and for the inverse rate ($dt/d\xi$).
- RDERIV Calculates estimates of the derivatives of relative rates of irreversible reactions with respect to reaction progress from backward finite differences. RDERIV evaluates the equation $(DRELRC) = (AKM)(RRF1)$ [a form of equation 8-5], where DRELRC is the array of derivatives, AKM is the matrix calculated by AKMATR, and RRF1 is the array of finite differences.
- RAFF Calculates the thermodynamic affinities driving the irreversible reactions (AFFRCT).

RSATCH Tests irreversible reactions for the saturation.

RTCALC Evaluates the rate laws that describe the rates of irreversible reactions. RTCALC returns all relevant rate functions.

INTEGR Integrates the finite-difference based truncated Taylor's series for a relative rate in order to calculate the advancement of an irreversible reaction over a step of reaction progress.

TIMER Integrates the finite-difference based truncated Taylor's series for the inverse rate ($dt/d\xi$) to calculate the time interval (DLTIME) corresponding to an interval of reaction progress (DELZI).

REACTS Computes the destroyed and current masses of the reactants and also calculates the current element totals in the "equilibrium" part of the system.

ZDIFF Directly evaluates finite-difference expressions (equation 8-4) for master variables as a function of reaction progress (. The results should be equivalent to those of TAYLOR, which evaluates the corresponding truncated Taylor's series representation. ZDIFF is used only in a debugging check (See IODB10, Chapter 5).

RDIFF Directly evaluates finite-difference expressions (equation 8-4) for relative reaction rates a function of reaction progress. The results should be equivalent to those of RTAYLR, which evaluates the corresponding truncated Taylor's series representation. RDIFF is used only in a debugging check (See IODB11, Chapter 5).

ALTERZ Alters the log K values of reactions according to NXMOD options specified on the INPUT file.

FLGSTZ Sets up the status flag arrays JSFLAG, JMFLAG, JKFLAG, JXFLAG, AND JGFLAG.

- SUPPRZ Suppresses species/reactions according to NXMOD options specified on the INPUT file.
- SCRIBE Writes the EQ6 PICKUP file.
- SERCH1 Finds the point of reaction progress at which a reactant is exhausted.
- SERCH2 Finds the point of reaction progress at which the mass of a secondary phase is maximized. SERCH2 supports the fluid-centered flow-through open system mode of calculation (NMODL1 = 3).
- SERCH5 Finds the point of reaction progress at which a secondary mineral phase disappears.
- SERCH6 Finds the approximate point at which a secondary mineral phase appears (just supersaturates the aqueous solution). This calculation is aimed at finding the point of reaction progress corresponding to the target affinity, AFTARG, which lies directly between the lower limit TOLSAT and the upper limit TOLSST.

APPENDIX C

IDENTIFICATION OF CODE AND DATA BASE VERSIONS

The activities of revising, extending, and maintaining computer programs and their data bases require some kind of 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 package. The part of the identification system that is internal to LLNL (but which might be followed elsewhere) has been modified from the scheme described previously (Wolery, 1983, Appendix H) in order to distinguish files for the CDC 7600 from their counterparts for the CRAY.

Package elements as defined here are codes or data files. Sample inputs and outputs that are included in software release packages (i.e., packages blessed for general use inside LLNL and distributed outside the Laboratory) are not generally treated as elements of the software packages. The identification scheme used for codes and data files is only applied to certain input/output test cases that are used in continuing code verification activities.

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 a time scale 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 made available for general use inside the Laboratory and distributed outside the Laboratory. New versions of the EQ3/6 package are periodically released. These are made available through the National Energy Software Center, Argonne National

Laboratory (NESC), 9700 South Cass Ave., Argonne, IL 60439 (Telephone 312-972-7250).

The release numbers increase in order and are chosen primarily so that they will not be easily confused in written or verbal communications. 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 Dec. 1981 release of EQ3/6 was EQ3/6.3175. Minor updates are designated by suffixing "B", "C", etc. to the release number.

To date, there have been six external releases of EQ3/6 and the following versions now exist.

<u>Version No.</u>	<u>Date</u>
2020	Feb. 1979
2055	Nov. 1979
3015	Dec. 1980
	Revised April 1981
3175	Dec. 1981
3175B	Sept. 1982
3230	Aug. 1983
3230B	Mar. 1984
3245	Sept. 1984

MCRT and its supporting files were released as the following independent package versions.

3175	Dec. 1981
3175B	Sept. 1982

There was no MCRT prior to the 3175 release. After the 3175B release, the MCRT package was folded into the EQ3/6 package.

The full name of a code or data file is its name, a period, the release number, a letter "U", and finally the stage number. For EQ5

this is illustrated by: EQ6.3245U01. This name is always given on the first line of a code or data file, along with the date. A short name eliminates the release number, taking it to be understood, e.g., EQ6U01. The letter U is retained in the short name only if the code or data file name ends in a number. For the MCRT code, the full name, MCRT.3245U01, shortens to MCRT01. Short names were formerly used to identify files on the LLNL computer system (Wolery, 1983, Appendix H). Full names and short names offer no indication whether the file is a CDC 7600 file or a CRAY file. They are purely "generic" in this sense.

Modified short names are now used to name files on the LLNL computer system. These names are restricted to a maximum of seven characters for files containing source code and eight characters for all others, including data files. When a code is compiled or loaded, the file produced is named by appending a letter to the source file name (See Appendix E), which accounts for the difference.

The stage number at the end of the file name is preceded by the letter "S" if the file is a 7600 file, and by the letter "C" if it is a CRAY file. The alphanumeric name of the code or data file is truncated to fit the remaining space (a maximum of four characters for source codes, of five for data files). Thus, EQ6U01 has the manifestation EQ6S01 on the 7600, and EQ6C01 on the CRAY. EQ3NR01 has the manifestations EQ3NS01 and EQ3NC01. The data file DATAOU01 has the manifestations DATAOS01 and DATAOC01. The release number for these files is implicit in either the release package they were obtained from or, at LLNL, from the directory chain-name they were stored under (See Appendix E).

Stage numbers identify day-to-day versions created during code or data base revision, development, etc. They are primarily meaningful only within LLNL. Sub-stage names may 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 a really bad editing goof. External release of a code package version usually terminates any 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., 3245 succeeds 3230) and the stage numbering goes back to 01. Note from the examples in the previous paragraph that stage numbers are intended to be machine-independent. They should not be incremented in adapting a file from the 7600 to the CRAY, or vice versa.

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 may extend for several stage-level versions before any attempt at testing is made.

APPENDIX D

RUNNING EQ6 AND RELATED CODES AT LLNL

The EQ3/6 software package is a set of geochemical modeling codes and supporting data files. The codes include EQTL, the thermodynamic data base preprocessor (Wolery, 1983), EQPITZ, the Pitzer data base processor (Wolery, 1984a), EQ3NR, the speciation-solubility code (Wolery, 1983), and EQ6, the reaction path code described in this document (See also Wolery, 1978, 1979). MCRT, a thermodynamic data base building code (Wolery, 1984b) and its own thermodynamic data files are now considered part of the EQ3/6 package, as they play an intimate role in supporting the EQ3/6 thermodynamic data base.

The EQ3/6 package is accessible at LLNL through the file storage routine XPORT. A package for CDC 7600 computers resides in the directory .977823.EQ3/6.3245.7600. A parallel package for the CRAY is in .977823.EQ3/6.3245.CRAY. These directories are write-protected. The 3245 in the chain-names refers to the release number of the package (See Appendix E). The contents of these directories include everything in the standard release packages sent outside the Laboratory- source codes, data files, sample inputs, and sample outputs- plus executable files for the codes.

There is very little difference between corresponding package elements for the CDC 7600 and the CRAY. There are slight differences in some of the sample outputs (including the secondary data files, e.g., DATA1, DATA3) because of the differences in word length on the two machines (60 bits on the 7600, 64 on the CRAY). There are only minor differences in the FORTRAN of the source codes (See Appendix F).

CRAY files do differ in format (character representation). A file in one machine format can be converted to the other format by using the utility TRANS. For example, to convert the data file DATAOS01 from 7600 format (implied by the "S" preceding the "01" stage number; See Appendix D), to CRAY format (where the "S" is replaced by a "C"), execute

```
TRANS I=(DATAOS01,7600),O=(DATAOC01,CRAY) / t v
```

To convert in the opposite direction, execute

```
TRANS I=(DATAOC01,CRAY),O=(DATAOS01,7600) / t v
```

Only files consisting of text, that is, source codes data files, inputs, and outputs are translatable. Binaries, executable files, libraries of relocatable code, etc., can not be translated in this fashion.

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 concern 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 EQ6 code, designated here as the file EQ6S01, use FTN to compile and load in one step:

```
FTN (I=EQ6S01,NALL,OPT=1,R=2,GLIB=EQLIS01B,PM,SET) / t v
```

The required input files are

EQ6S01	EQ6 source code
EQLIS01B	binary version of the EQLIB library*

The output files are

EQ6S01B	binary file
EQ6S01L	compilation listing
EQ6S01M	load map
EQ6S01X	executable file

The executable file is the only one of the above then 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 EQ6 as an example:

```
CFT I=EQ6C01,B=EQ6C01B,L=EQ6C01L / t v
```

Then input EQ6C01B and EQLIC01Q** to the loader LDR:

```
LDR I=EQ6C01B,X=EQ6C01X,ML=EQ6C01M,LIB=EQLIC01Q,LIB=FORTLIB / t v
```

*To create this library on the 7600, compile the source code with FTN:

```
FTN (I=EQLIB01,B=EQLIB01B,OPT=1,R=2) / t v
```

**The binary file EQLIC01B can not be directly used as a library on the CRAY. To create EQLIC01Q, first compile with CFT and then use BUILD:

```
CFT I=EQLIC01,B=EQLIC01B / t v
```

```
BUILD NL=EQLIC01Q,B=EQLIC01B / t v
```

To execute a code, you need the corresponding executable file and the requisite data and input files. To execute EQ6, where EQ6S01X is the controlee file, type

```
EQ6S01X / t v
```

You must provide the necessary data and input files. Here they are DATA2, DATA3, and INPUT. The files produced are OUTPUT, PICKUP, and the TAB files TABA, TABB, etc.

File names may be equivalenced on the execute line. For example, if the INPUT file is named I5RCTS, the user may enter

```
EQ6S01X INPUT=I5RCTS / t v
```

Multiple specifications are often very useful, e.g.,

```
EQ6S01X INPUT=I5RCTS,OUTPUT=O5RCTS,PICKUP=P5RCTS / t v
```

APPENDIX E

FORTRAN CONVENTIONS, CODE PORTABILITY, FIELD LENGTHS, AND REDIMENSIONING

The ease of portability of a FORTRAN code can be greatly improved by certain restrictions and conventions. This section describes those that have been adopted in developing the codes in the EQ3/6 package. These conventions (slightly extended from those described by Wolery, 1983, Appendix I) were adopted in the light of experience in transferring these codes to CRAY, UNIVAC, IBM, and VAX machines.

1. All common blocks appear in the main program. Commented out symbolic common blocks also appear here to aid in redimensioning.
2. Variable and subroutine names are restricted to six characters.
3. Character information is stored at six characters per word. This pertains to variables beginning with the letter U (See below). The writer recommends adopting eight characters per word to readers looking to adopt FORTRAN standards for other software projects.
4. The following type conventions apply to the first letter of a variable name. Absolutely no exceptions are permitted.
 - (a) I, J, and K: INTEGER
 - (b) L and M: REAL on 60 and 64 bit machines, REAL*8 on 32 bit machines
 - (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 machines)

(e) all others: REAL on 60 and 64 bit machines, REAL*8 on 32 bit machines

5. One statement per line.

6. All labels are numeric; none are alphabetic or alphanumeric

7. No IF-THEN-ELSE constructions. These constructions are the major difference between FORTRAN 77 (FORTRAN V) and FORTRAN 66 (FORTRAN IV). This restriction is not recommended for other software projects. It may be relaxed in the near future for EQ3/6 development.

8. No arithmetic IF statements.

9. No constants in subroutine argument lists. This prevents certain kinds of conflicts in 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.

10. Character string variables are initialized only by either reading from a file or in DATA statements. Use

```
DATA UVAR/"ENDIT. "/  
:  
:  
IF (UDUM.NE.UVAR) GO TO 235
```

not

```
IF (UDUM.NE."ENDIT. ") GO TO 235
```

11. 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
```

The FORTRAN source code in EQ6 is designed to maximize portability among different machines. Essentially the same source code works on all machines, thanks to the above conventions. However, there are some differences that should be pointed out. On the CDC 7600, some of the COMMON blocks must be allocated to Large Core Memory (LCM) by means of LEVEL 2 declarations. These declarations should be commented out in adapting the 7600 source code to other machines. This is done at LLNL by putting the pattern "C7600" beginning in column one of the affected lines. This may be seen in the CRAY source code, for example.

Other differences pertain to the opening and closing of files, testing for end-of-file, and getting the date and time from the operating system. The user is more or less stuck with having to deal with these differences in adapting the program to other machines. In the 7600 source codes, a good way to find all the occurrences of such machine-dependent references is to do a search on the pattern "CCRAY" to find all the CRAY adaptations that have been commented out. In the CRAY source code, a similar search may be made on the pattern "C7600."

Some VAX adaptations may be found by searching on the pattern "CVAX." EQ6 contains some special coding in subroutine PATH which avoids overflow problems in the calculation of finite difference functions if the pertinent lines are activated by removing the "CVAX" pattern.

EQ6.3245U01 is dimensioned to handle up to:

NCTMAX: 40 chemical elements
NSQMAX: 80 aqueous master species (strict plus auxiliary basis species)
NSTMAX: 300 aqueous species (total)
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: 20 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 335,000B 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 147,000B words.

To aid in redimensioning any of the EQ3/6 codes, including EQ6, 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 these. 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,NSTMAX),  
C   $ CDRST(NRSTMX)
```

is given in the main program of EQ6.3245U01 to indicate the proper dimensions corresponding to

```
COMMON CDRS(42,259),CESS(40,300),CDRST(259)
```

Users are strongly advised to use global pattern replacement techniques as the exclusive means of code redimensioning, because even 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 used very effectively for this purpose.