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CALCULATION OF CHEMICAL EQUILIBRIUM BETWEEN AQUEOUS SOLUTION AND MINERALS: THE EQ3/6 SOFTWARE PACKAGE

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CALCULATION OF CHEMICAL EQUILIBRIUM BETWEEN AQUEOUS SOLUTION AND MINERALS: THE EQ3/6 SOFTWARE PACKAGE

ABSTRACT

The newly developed EQ3/6 software package computes equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict the consequences of heating and cooling aqueous solutions and of irreversible reaction in rock-water systems. The programs are valuable for studying such phenomena as the formation of ore bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste.

EQ3 and EQ6 are compared with such well-known geochemical codes as SOLMNEQ, WATEQ, REDEQL, MINEQL, and PATHI. The data base allows calculations in the temperature interval 0-350°C, at either 1 atm-steam saturation pressures or a constant 500 bars. The activity coefficient approximations for aqueous solutes limit modeling to solutions of ionic strength less than about one molal.

The mathematical derivations and numerical techniques used in EQ6 are presented in detail. The program uses the Newton-Raphson method to solve the governing equations of chemical equilibrium for a system of specified elemental composition at fixed temperature and pressure. Convergence is aided by optimizing starting estimates and by under-relaxation techniques. The minerals present in the stable phase assemblage are found by several empirical methods. Reaction path models may be generated by using this approach in conjunction with finite-differences. This method is analogous to applying high-order predictor-corrector methods to integrate a corresponding set of ordinary differential equations, but avoids propagation of error (''drift'').

INTRODUCTION

This report describes the EQ3/6 software package for computing chemical equilibrium problems in aqueous geochemistry. The package includes two principal source codes, EQ3 and EQ6. Data files support model calculations in the temperature interval 0-350°C, either at pressures on the 1 atm-steam saturation curve or at a constant pressure of 500 bars. The activity coefficient approximations for aqueous species are not suitable to describe aqueous solutions of concentration greater than about 1 molal ionic strength.

EQ3 computes from input analytical data the distribution of chemical species (ions, neutral species, ion-pairs, and complexes) in an aqueous solution. This calculation produces a model of the fluid, which specifies the concentration and thermodynamic activity of each chemical species occurring in the chemical system and included in the data base. The program then calculates the saturation state of the fluid with respect to all relevant mineral phases in the data base. The aqueous solution model calculated by EQ3 is used as a starting point for mass transfer computations by EQ6.

EQ6 can compute several kinds of mass transfer models. If the initial model fluid is supersaturated with respect to any mineral phases, the program first ''equilibrates'' it by calculating a new model of modified fluid plus precipitates. This new model satisfies the original mass constraints. EQ6 then computes reaction progress models of compositional evolution and mass transfer in a closed or open (flow-through) system containing this aqueous solution (with or without any initial precipitates). Reaction progress may describe changes in temperature and pressure, irreversible reaction of the fluid with reactants (rocks, minerals, gases), or both of these simultaneously. The calculation predicts in detail the changes in fluid composition, the identity, appearance, and disappearance of secondary minerals, and the values of reaction progress at which the fluid saturates with reactants. Such computations permit modeling of the effects of heating and cooling aqueous solutions and of irreversible reaction in rock-water systems. They represent a powerful tool to study such phenomena as the formation of ore bodies, scaling and plugging in geothermal development, and the long-term isolation of nuclear waste forms. Two simple examples, the dissolution of microcline ($KAlSi_3O_8$) in HCl solution at 25°C and 1.013 bars and the heating of Salton Sea water, illustrate use of the programs.

The total EQ3/6 software package consists of the two principal source codes (EQ3 and EQ6), the set of supporting data files, two utility routines for data file management, and sample input files for EQ3 and EQ6. The package contents are listed in Appendix A; the length of the package precludes reproducing all of its contents. However, this software is available from the National Energy Software Center.* The EQ3/6 package consists of over 30,000 card images and should therefore be requested only on magnetic tape. A request form is reproduced in Appendix B.

All source codes were written in FORTRAN Extended 4.6 language (Control Data Corporation, 1977) for execution on CDC 6600 and 7600 computers. Principal programs EQ3 and EQ6 and utility program EQF each require one or more externals (subroutines) from the International Mathematical and Statistical Library, a set of commercial software subscribed to by most government and university computing centers in the United States. Also, it is desirable but not necessary to incorporate a local external into EQ6 to permit the program to sense the approach to the job-computing limit during execution. Activation of this feature permits EQ6 to write a file that permits re-starting the job.

The purposes of this report are to announce the availability of the EQ3/6 software package, to discuss the application of EQ3 and EQ6 to solving problems in aqueous geochemistry, to compare these with other available programs, and to present the mathematical and numerical approaches adopted in program EQ6. The source codes and data files of this package were written to be highly transparent to the user. Each program has its own operating manual built into the source code via comment statements. Each manual is the primary documentation for each program, giving a general overview of its purpose, technical parameters, and other information the user needs to operate and even modify the program. This document is therefore intended to supplement, not duplicate, these operating manuals.

CAPABILITIES OF PROGRAMS EQ3 AND EQ6

The first principal program of the package, EQ3, solves the distribution-of-species problem familiar to geochemists: given certain compositional parameters of an aqueous solution, what are the concentration and thermodynamic activity of each individual ionic or molecular species (e.g., Na^+, $NaSO_4^-$, $NaCl^{\circ}$)? Parameters used in such problems are the "total" concentrations of simple species (i.e., "total" Na^+), the pH, and the oxidation-reduction potential (Eh) or some other redox parameter such as oxygen fugacity or pe^-. The geochemical foundation of this problem has been discussed in detail by Garrels and Christ (1965, Ch. 4). The most closely comparable programs now available are SOLSAT (Helgeson *et al.*, 1970), SOLMNEQ (Kharaka and Barnes, 1973), and WATEQ (Truesdell and Jones, 1974) and its daughter versions WATEQF (Plummer *et al.*, 1976) and WATEQ2 (Ball *et al.*, 1979). The programs REDEQL (Morel and Morgan, 1972) and its daughter MINEQL (Westall *et al.*, 1976) are also roughly similar.

I shall term this distribution-of-species calculation a Class I problem to distinguish it from related chemical equilibrium computations (Class II) that are defined by a complete array of mass balance constraints. This Class I calculation has no mass balance constraints on the elements oxygen and hydrogen, which compose the solvent, water. In place of such constraints, pH and Eh values are fixed and the modeled system contains a completely arbitrary mass of solvent (the species $H_2O_{(\ell)}$), which, adopting the molal scale of concentration, may conveniently be taken as 1000 g. The input variables (pH, Eh, etc.) are such that the masses of oxygen and hydrogen in the system (relative to 1000 g of solvent) is determinable only after the Class I computation has been solved by an iteration process.

The second principal program, EQ6, computes models discussed by Helgeson (1968, 1979) for chemical equilibrium and mass transfer in aqueous systems. It is similar in modeling function to the program PATHI (a.k.a.

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*Write to the National Energy Software Center, Attn. M. Butler, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

PATHCALC: Helgeson, 1968; Helgeson *et al.*, 1970), but differs in numerical methodology in that, unlike PATHI, it does not integrate a set of differential equations. Helgeson's model of partial-equilibrium mass transfer allows division of the aqueous system into an equilibrium subsystem (aqueous solution plus minerals with which it is in heterogeneous equilibrium) and a reactant subsystem (another aqueous solution or a set of minerals that are not in equilibrium with the solution in the first subsystem). The reactant components are then titrated into the equilibrium subsystem according to a reaction progress variable (ξ) and specified relative rate constants. Temperature and pressure may be constant or functions of ξ.

At any value of ξ, however, the problem reduces to finding the distribution of phases and species in an aqueous system at fixed temperature, pressure, and known mass for each element present. This requires a Class II calculation. Remember that, unlike the Class I computation, it is constrained by a mass balance relation on each element in the system, including oxygen and hydrogen. In this case, the mass of the solvent is no longer arbitrary, but must be calculated. Similarly, the pH and Eh (or alternate redox parameter) are now output, not input, variables.

The Class I calculation yields the thermodynamic affinity of solid phase components to precipitate (i.e., the saturation state of the aqueous solution with respect to the various minerals). This is usually the main goal of such computations. However, a Class I calculation does not reveal which of the (often many) supersaturated phases would actually be present in a stable heterogeneous assemblage. In fact, such an assemblage can include a phase with which the initial aqueous solution is undersaturated. This is clearly a Class II problem, because the pH, Eh, and mass of solvent all may change in response to precipitation.

Program EQ3 was written mainly to provide input to EQ6 by calculating a model of the initial aqueous system, though it can also be used independently, as other Class I programs such as SOLMNEQ are. EQ3 is very flexible in the input constraints it accepts, which may include "total" concentrations, "free" concentrations, activities (pH), and assumptions of heterogeneous (aqueous solution-mineral) equilibria. The user may define the redox state directly by specifying a value of Eh, pe^-, oxygen fugacity, or dissolved oxygen content, or indirectly by specifying information on a redox couple (e.g., by entering values for both "total" sulfate and "total" sulfide).

EQ3 allows specification of redox disequilibrium if the user has sufficient input to do so. Ion-pairing and complexing reactions of geochemical importance are thought to be sufficiently rapid that the equilibrium assumption is appropriate for treating them (Garrels and Christ, 1965, Ch. 4). However, it is not generally appropriate in the case of redox reactions, especially at low temperatures, because many of these reactions are controlled by bacterial activity. Thus, a natural aqueous solution may yield analyses of dissolved oxygen, "total" sulfate, and "total" sulfide that give one calculated value of Eh for the oxygen-water couple and a different value for the sulfate-sulfide couple. A direct measurement with a platinum electrode might give still a third value. EQ3 thus permits calculation of a more realistic chemical model when sufficient input data are available.

EQ6 first checks that the input system (usually defined relative to 1000 g of solvent) is in homogeneous equilibrium. If it is not, the program first "equilibrates" it according to the specified mass balance constraints. This will yield a single Eh for the solution and alter to some extent all the other solution parameters, including the pH. If there are then any supersaturated phases, the program "precipitates" a set so that no supersaturations remain. This step may result in still different values for the pH and other solution parameters. Any such "initial" precipitates may be retained in the system or deleted before the reaction progresses. Calculations may then be performed to model simple titration or irreversible reaction with "reactants" in systems that are either closed to solids or open (flow-through systems). Such models will be discussed later.

EQ6 and EQ3 are supported by a data base that covers the temperature range 0-300°C over one of two pressure regimes. One set of data files is for a constant pressure of 1 atm (1.013 bar) from 0-100°C and the steam saturation curve from 100-300°C; the other set is for a constant pressure of 500 bars. Another set of data files holds log K (equilibrium constant) values for specified reactions at temperatures of 0, 25, 60, 100, 150, 200, 250, and 300°C. EQ3 and EQ6 do not read any of these files directly, but rather a set of secondary files which contain fitted coefficients of interpolating polynomials. Two polynomials are regressed for each reaction in the data base: one for 0-100°C, the other for 100-300°C. The 100°C point is weighted in the regression to minimize any discontinuity between the two polynomials at that temperature. More details of the data base are given in Appendix C.

EQUILIBRIUM CALCULATIONS IN AQUEOUS GEOCHEMISTRY

Equilibrium calculations are of interest to many fields, such as chemical engineering and physiological chemistry; new notes or articles on such computations appear almost monthly in the scientific literature. A review of the past progress in applying equilibrium calculations to problems of aqueous solution chemistry will aid evaluation of EQ3 and EQ6 in light of previous methods. This short review is restricted to important works that either lie in the field of aqueous geochemistry or deal with methods or concepts pertinent to the EQ3/6 software package.

NATURE OF CHEMICAL EQUILIBRIUM PROBLEMS

Solving a chemical equilibrium problem requires three general steps. First, one must explicitly define the model in terms of its physical and thermodynamic nature. For example, the "classical" problem in chemical equilibrium computations is to calculate the state of a closed system of specified elemental composition at fixed temperature and pressure (i.e., the Class II problem solved by EQ6 for aqueous systems). A different closed system model might specify fixed pressure and enthalpy, so that the temperature is an unknown variable to be calculated. Open systems of various kinds are another family of possible models. The nature of the physical-chemical model determines the set of governing equations to be used in computations.

The second step is to manipulate this original set of equations into a desirable form. This usually reduces the number of operating variables (unknowns) in the computation. The original governing equations may contain many parameters with unknown values, including masses, concentrations, and non-ideality parameters. The manipulation is usually done so that one need deal only with the masses of a subset of species or, alternatively, with extent-of-reaction variables for a set of linearly independent reactions. The third step is to solve the remaining simultaneous equations. Iterative techniques are required except in the case of trivial problems (see Zeleznik and Gordon, 1968; Van Zeggeren and Storey, 1970).

Rather than solving sets of equations, some workers have chosen to formulate the equilibrium computation as an optimization problem, such as solving the so-called classical problem by minimizing the calculated free energy of the system (see Van Zeggeren and Storey, 1970, for a detailed discussion of this approach). However, not all equilibrium problems of interest are properly constrained by an optimization criterion (e.g., the Class I distribution-of-species problem). Most geochemists have avoided optimization techniques in favor of solving sets of nonlinear equations.

The techniques for solving systems of equations have been grouped by Van Zeggeren and Storey (1970, p. 134) into three categories: (1) pure iteration; (2) Newton-Raphson iteration; and (3) integration of ordinary differential equations.

Pure iteration is basically simple recursion or back-substitution. The arrangement of the recursion scheme is often critical to getting the system to converge. This method gives first-order convergence in the limit of the solution.

The Newton-Raphson method is probably the most popular device for solving systems of nonlinear equations; a detailed discussion of this approach can be found in Van Zeggeren and Storey (1970) or any general text on numerical methods. It gives second-order convergence in the limit of the solution. However, this should not be interpreted to mean that this method is necessarily faster than pure iteration.

The differential equations approach, not often used, is to differentiate the governing algebraic equations with respect to a variable that controls the composition of the system. The basic concept is to first use one of the other methods to solve for the state of a system that contains all the necessary elements, but in relative proportions that make the problem easy to solve. One then integrates the system of ordinary differential equations to the system composition that was actually desired.

DEVELOPMENT OF MODELS FOR AQUEOUS SYSTEMS

Methods for calculating chemical equilibrium models of non-trivial systems were first developed by engineers and applied mathematicians in the 1940's. They successfully applied such computations to the development of rocket propellants, explosives, and sophisticated chemical processing techniques. The physical systems they studied usually consisted of a single gas phase or, less often, a gas phase plus one or more solids. These computations were nearly always what I term Class II problems, because they typically included a mass balance constraint on each element in the system. The basic strategies for computing chemical equilibrium models in such systems have been reviewed extensively by Zeleznik and Gordon (1968) and by Van Zeggeren and Storey (1970).

In the early 1960's, biochemists began to apply equilibrium models to the study of physiological fluids (see Perrin, 1965). These, unlike the earlier models, were basically Class I computations. This work inspired Garrels and Thompson (1962) to develop a pioneering model of sea water, which included the first distribution-of-species calculation in the field of geochemistry. Such calculations have since been applied to a wide variety of natural waters (e.g., Garrels and Christ, 1965, Ch. 4; Polzer and Roberson, 1967; Paĉes, 1969).

The biochemists and geochemists generally avoided the numerical aspects of thermodynamic equilibrium problems. Most of the geochemists used the pure iteration method: simple back-substitution schemes patterned after that of Garrels and Thompson (1962), which was originally intended for hand calculation. The sophisticated numerical analysis and techniques developed by applied mathematicians and engineers were largely ignored. Simple back-substitution is the numerical basis of such well-known programs as SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ (Truesdell and Jones, 1974). The usual alternative to back-substitution in solving Class I problems is the Newton-Raphson method, which is used in the well-known programs REDEQL (Morel and Morgan, 1972) and its daughter MINEQL (Westall *et al.*, 1976). It was also adopted by Crerar (1975) for modelling hydrothermal solutions. The Class I problem usually does not present any formidable numerical difficulties, and from the practical viewpoint there appears to be no one superior program or method (see Nordstrom *et al.*, 1979).

The geochemists' distribution-of-species problem is often set up so that the mass action relations describing complex dissociation and redox crosslink reactions are substituted for mass and charge balance in the original equations. This reduces the number of unknown species concentrations, which must be iteratively calculated, to a so-called "basis" set. Each basis species may be assigned a formal one-to-one association with a mass balance relationship in which its concentration appears. Usually, the basis species is a simple ion, and one assigns Na^+ to sodium mass balance, for example. For a model with redox reactions, oxygen fugacity or Eh or pe^- may be the logical choice as the basis species to associate with the charge balance equation. (If a model contains no redox reactions, charge balance is implicitly constrained by the mass balance relationships.) Basis sets are sometimes formally recognized (as for example in the MINEQL program of Westall *et al.*, 1976). However, they are also present implicitly in the back-substitution method of Garrels and Thompson (1962).

Program EQ3 has a formally recognized set of basis species which is presently fixed by the structure of its data base. The choice of basis set is sometimes crucial in a distribution-of-species calculation, however. It is especially so when dealing with trace metals or ligands for which the mass balance is heavily dominated by a species not in the basis set. In such cases, the iteration may converge at an impractically slow rate or simply diverge. One may solve the problem by choosing the dominant species, whether a simple ion of alternate oxidation state or a complex, as the basis species. MINEQL (Westall *et al.*, 1976) is an example of a code that changes its basis set to influence the iteration to converge. Such a feature has not yet been incorporated into EQ3.

The first step toward computation of Class II models for aqueous systems was made by Helgeson (1968). He developed a partial equilibrium model for the irreversible reaction of an aqueous system (aqueous solution plus minerals, all in heterogeneous equilibrium) with a set of "reactant" minerals, whose relative rates of dissolution were specified in terms of a single reaction progress variable ξ. The initial aqueous system (consisting of only an aqueous solution) was first modeled by a Class I calculation using the program SOLSAT (Helgeson *et al.*, 1970) as a subroutine.

Helgeson used the differential equations approach; he differentiated with respect to ξ the set of equations describing mass and charge balance and mass action. Derivatives with respect to ξ of the unknown quantities in the resulting set of linear differential equations could be found by solving a matrix equation. A second differentiation permitted similar evaluation of the second derivatives. The overall (irreversible) reaction could then be computed for a step of reaction progress by using these values of the first and second derivatives to evaluate a truncated Taylor's series. At completion of each such step, the results were checked to see if any mineral supersaturations had developed or if any "product" minerals (solids in equilibrium with the fluid) had "disappeared" (decreased to less than a very small, arbitrary mass). If either condition was detected, the step-size was cut by an interval-halving technique to find the lowest value of reaction progress at which a new phase saturated or an old one "disappeared." The assemblage of "product" minerals was then modified and the integration continued. This permitted prediction of the overall mass transfer in the system, including changes in fluid chemistry, the appearance and disappearance of "product" minerals, and the eventual equilibration of the fluid with the "reactant" minerals.

Helgeson's computer program (PATHI; a.k.a. PATHCALC) was a pioneering effort in theoretical geochemistry. It was used to generate models of geochemical processes such as diagenesis and metasomatism (Helgeson *et al.*, 1969) and genesis of ore-bearing fluids (Helgeson, 1970). It is methodologically interesting as one of the few reported examples of the differential equations approach to equilibrium computation. PATHI, however, had several deficiencies. First, if the initial solution created by the Class I computation was supersaturated with respect to any minerals, the method could not be applied and the program was forced to terminate. Secondly, ''drift'' error developed and propagated in the integration of the differential equations because of the higher-order terms neglected in the truncated Taylor's series. Third, execution was long and costly. The last problem has been remedied by adopting the high-order predictor-corrector integration method described by Gear (1971 a,b), as was done in a version of PATHI developed at Los Alamos Scientific Laboratory (Herrick, 1976).

Russian investigators (Karpov and Kaz'min, 1972; Karpov *et al.*, 1973) criticized PATHI for the first two reasons noted above. They eliminated these problems by adopting the free energy minimization method (the optimization technique mentioned earlier) developed by one school of engineers (see Van Zeggeren and Storey, 1970). Their efforts, however, seem to have been largely ignored in the West.

Reed (1977) has recently written a Class II program that uses the Newton-Raphson method to solve the governing algebraic equations and thereby avoids the ''drift'' problem. He has applied this code to modelling the generation of ore-forming fluids and ore bodies.

The programs REDEQL (Morel and Morgan, 1972) and its daughter MINEQL (Westall *et al.*, 1976) deserve comment here because they have the capability to calculate the models of heterogeneous aqueous systems. However, they appear to do so by means of Class I, not Class II, computations. If calculation by either of these programs shows the aqueous solution to be supersaturated with respect to a solid, the mass action equation corresponding to dissolution of that solid is used in a substitution to eliminate one mass balance relation. However, no mass balance constraints are recognized in the first place for the elements oxygen and hydrogen, the solvent components. This means that the mass of the solvent plus either the pH or the Eh, or both, must remain fixed during the ''precipitation.'' Therefore the results of such calculations do not correspond to the physical situation in which a supersaturated solution in a closed environment converts to a stable heterogeneous assemblage of modified, saturated fluid plus precipitates. Another difficulty with REDEQL and MINEQL is that they sometimes make use of a parameter called ''total ionizable hydrogen'' (a.k.a. TOTH; Morel and Morgan, 1972). The definition of this parameter is a reduced form of the charge balance equation. Unfortunately, TOTH is not a conserved quantity in the presence of redox reactions, so it cannot be used to compute pH or pe^- as can the charge balance equation itself.

EQ6, with its companion program EQ3, was written to perform the modelling functions of PATHI while eliminating its shortcomings and extending its flexibility for the user. EQ6 solves at each point of reaction progress the original algebraic equations that describe mass and charge balance, mass action, and non-ideality. Finite-difference expressions of high order are used to estimate derivatives with respect to reaction progress and then predict the values of a basis set of unknowns at a subsequent point of reaction progress. This process is closely analogous to the predictor part of Gear's (1971 a,b) scheme for integrating differential equations. However, the predicted values are then corrected, by using the Newton-Raphson method, to satisfy the original algebraic equations instead of corrected to (locally) satisfy the difference equations that represent the corresponding differential equations. This process avoids incurring a ''drift'' error. The Jacobian matrix used by EQ6 in the correcting iteration is the same as Helgeson's ''grand'' matrix (for constant temperature and pressure), which is used in correcting when using the differential equations approach. The operational difference between my method and Helgeson's is that the matrix equations are then solved with different right-hand-side vectors.

The methods used in EQ3 have been discussed in detail by Wolery and Walters (1975) and were used in a computer program called SALT (Walters and Wolery, 1975). This document will therefore concentrate on presentation of the mathematical derivations used in EQ6 and discussion of some of the important numerical techniques adopted.

APPLYING THE NEWTON-RAPHSON METHOD TO THE CLASS II EQUILIBRIUM CALCULATION

BASIC DEVELOPMENT

The basic strategy in program EQ6 is to solve for the equilibrium distribution of phases and species present in a closed system ($\tilde{E}$ the equilibrium subsystem) for specified elemental compositions ($n^t_\epsilon, \epsilon = 1, \hat{\epsilon}$) at fixed temperature (T) and pressure (P). (See the glossary of symbols.) The only additional restriction is that an aqueous phase be present. Tables 1-3 contain the set of equations required to describe this model. With the glossary of symbols, these equations introduce the notation, which is somewhat complicated. The equations will be manipulated into a form suitable for solving by the Newton-Raphson method.

Glossary of Symbols

ϵ	subscript denoting a chemical element
$\hat{\epsilon}$	total number of chemical elements
s	subscript denoting an aqueous species ($1 = H_2O_{(\ell)}$)
w	special subscript denoting $s = 1$ ($H_2O_{(\ell)}$)
$\tilde{s}$	number of aqueous species used as basis variables to describe the aqueous phase; refers in particular to the fictitious species $O_{2(g,aq)}$
$\dot{s}$	number of non-fictitious aqueous species basis variables; identical to $\hat{\epsilon}$ and $\tilde{s} - 1$
s*	subscript denoting the aqueous species destroyed in the r-th aqueous reaction; $\tilde{s} < s^* \leq \hat{s}$
$\hat{s}$	total number of aqueous species
r	subscript denoting an intra-aqueous reaction (dissociation of an aqueous complex or redox cross-link reaction)
$\hat{r}$	total number of (independent) intra-aqueous reactions; note that $\hat{r} = \hat{s} - \tilde{s}$
ϕ	subscript denoting a pure mineral (one having a fixed composition) or its dissolution reaction
$\hat{\phi}$	total number of pure minerals; also denotes osmotic coefficient
ψ	subscript denoting a solid solution
$\hat{\psi}$	total number of solid solutions
χ	subscript denoting a solid-solution end-member component or its dissolution reaction
$\hat{\chi}$	total number of end-members of a solid solution
n	mass of a species, in moles
n^t_ϵ	total mass of the ϵ-th element
ℓ	$\log_{10}$ n; logarithmic mass
z_s	electrical charge on the s-th aqueous species
m_s	molal concentration of the s-th aqueous species; note that $m_s = \omega n_s/n_w$
γ_s	activity coefficient of the s-th aqueous species
a	thermodynamic activity
x	mole fraction of a solid-solution end-member
λ	activity coefficient of a solid-solution end-member
I	true ionic strength

$\tilde{I}$	equivalent stoichiometric ionic strength of a sodium chloride solution; defined as the total molality of either Na or Cl
$f_{O_{2(g,aq)}}$	fugacity of oxygen in the aqueous phase; may be abbreviated as f_{O_2}
$\mathring{a}$	Debye-Huckel ion size parameter
$A, B, \dot{B}$	Debye-Huckel parameters
c_1, c_2, c_3, c_4	power series coefficients for computing $\gamma_{CO^0_{2(aq)}}$
b_1, b_2, b_3, b_4	coefficients for computing $a_{H_2O_{(\ell)}}$
R	gas constant (1.98726 cal/mol−K)
T	temperature−K
2.303	ln 10
ω	water constant; 1000/molecular weight of $H_2O \approx 55.51$
k	composition coefficient (moles element per formula weight)
ν	reaction coefficient
G_{xs}	excess Gibbs energy of a solid-solution
W	solid-solution excess free energy parameter
C_w	abbreviation for $d \log a_w / d \tilde{I}$
C_s	abbreviation for $d \log \gamma_s / d I$
$S_{\chi=i,\chi=j}$	abbreviation for the formal partial derivative $\partial \log \lambda_{\chi=i} / \partial \log x_{\chi=j}$
K	equilibrium constant of a reaction
Q	activity product of a reaction $\equiv \prod_{i} a_i^{\nu_i}$
$\underline{z}$	vector of basis variables which describes a system or subsystem in internal equilibrium
$\underline{\alpha}$	vector of residual elements which measures the error in the vector $\underline{z}$
$\underline{\beta}$	residual vector identical to $\underline{\alpha}$, except that the mass balance residual elements are in the relative, rather than the absolute, sense
β_{max}	the largest magnitude (absolute value) of any element of $\underline{\beta}$
β_{rms}	the root-mean-square of the elements of $\underline{\beta}$
$\underline{\delta}$	vector of Newton-Raphson correction terms
δ_{max}	the largest magnitude of any element of $\underline{\delta}$
$\underline{\underline{J}}$	the Jacobian matrix $(\partial \alpha_i / \partial z_j)$
κ	relaxation parameter
β_{conv}	convergence function; see text
δ_{conv}	alternate convergence function; see text
Δ	decision function for dropping a phase; see text
$\tilde{E}$	a closed system in internal equilibrium
$\tilde{R}$	a system containing a set of one or more reactants
$\tilde{V}$	a system conceptually defined as a closed reaction vessel
$\tilde{X}$	a system "physically removed" from $\tilde{E}$; mineral phases are periodically removed from $\tilde{E}$ to $\tilde{X}$ in open system calculations
ξ	reaction progress variable
$\Delta\xi$	increment of reaction progress
P	pressure, in bars

T^c	temperature—°C
T_0^c	temperature at $\xi = 0$—°C
t_1, t_2, t_3	temperature tracking coefficients
ρ	subscript denoting a reactant
$\hat{\rho}$	total number of reactants
ξ_1, ξ_2, ξ_3	reactant tracking coefficients for the input of a reactant into the system $\widetilde{E}$; relative rate constants of order increasing from 1
$f[\xi_1, \xi_2, \ldots, \xi_n]$	n-th order finite difference for a set of reaction progress values
$f[12 \ldots n]$	condensed notation for n-th order finite difference
$\underline{f}$	vector of finite differences increasing in order from 1
$\underline{d}$	vector of derivatives with respect to reaction progress increasing in order from 1
$\underline{\underline{D}}$	matrix for computing $\underline{d}$ from $\underline{f}$; $\underline{d} = \underline{\underline{D}}\,\underline{f}$

These equations are written in a format that assumes a specific notational organization of the aqueous species ($s = 1, \hat{s}$). The first $\dot{s}$ species ($s = 1, \dot{s}$; $s = 1$ denotes $H_2O_{(\ell)}$) correspond on a purely formal one-to-one basis with the elements and their mass balance equations. I have chosen to adopt oxygen fugacity as the redox parameter used in writing reactions. To index this variable, I shall create a fictitious aqueous species, $O_{2(g,aq)}$, and denote it as the $\widetilde{s}$-th species ($\widetilde{s} = \dot{s} + 1$). It may be assigned a formal correspondence with the charge balance equation. The remaining aqueous species ($s = \widetilde{s} + 1, \hat{s}$) correspond one-to-one with the aqueous reactions in which they are destroyed. The first $\widetilde{s}$ aqueous species are the ''basis'' species. Each reaction, whether it is a dissociation, redox crosslink, or mineral or gas dissolution reaction, is written exclusively in terms of these basis species and the associated species (aqueous, solid, or gas) that is destroyed:

$$0 \rightleftarrows \nu_{rs^*}(s^*) + \sum_{s=1}^{\tilde{s}} \nu_{rs}(s)$$

(e.g., $0 \rightleftarrows -CaCO_3^o + Ca^{++} + CO_3^{=}$,

$0 \rightleftarrows -Fe^{+++} - 1/2\ H_2O_{(\ell)} + Fe^{++} + H^+ + 1/4\ O_{2(g,aq)}$)

$$0 \rightleftarrows \nu_{\phi\phi}(\phi) + \sum_{s=1}^{\tilde{s}} \nu_{\phi s}(s)$$

$$0 \rightleftarrows \nu_{\chi\psi\chi\psi}(\chi\psi) = \sum_{s=1}^{\tilde{s}} \nu_{\chi\psi s}(s)$$

(e.g., $0 \rightleftarrows -KAlSi_3O_8 - 4\ H^+ + Al^{+++} + 3\ SiO_2^o + H_2O_{(\ell)}$)

Table 1. Equations defining a chemical equilibrium problem for a system that consists of an aqueous phase and solid phases and for which the total mass of each element (n_ϵ^t) is specified.

Mass balance for each element ($\epsilon = 1,\hat{\epsilon}$)

$$n_\epsilon^{t} = \sum_{s=1}^{\hat{s}} k_{\epsilon s} n_s + \sum_{\phi=1}^{\hat{\phi}} k_{\epsilon\phi} n_\phi + \sum_{\psi=1}^{\hat{\psi}} \sum_{\chi=1}^{\hat{\chi}_\psi} k_{\epsilon\chi\psi} n_{\chi\psi}$$

$$(\text{e.g., } n_s^{t} = n_{SO_4^=} + n_{FeSO_4^{o}} + n_{FeSO_4^{+}} + n_{HS^-} + n_{s^=} + 2n_{FeS_2(pyrite)})$$

Charge balance in the aqueous phase

$$0 = \sum_{s=2}^{\hat{s}} z_s n_s$$

Mass action for intra-aqueous reactions (complex dissociation and redox cross-link reactions); $s^* > \tilde{s}$ denotes the species destroyed in the r-th reaction ($r = 1,\hat{r}$)

$$K_r = a_{s^*}^{\nu_{rs^*}} f_{O_2}^{\nu_{r\tilde{s}}} \prod_{s=1}^{\dot{s}} a_s^{\nu_{rs}}$$

Mass action for minerals of fixed composition ($\phi = 1,\hat{\phi}$)

$$K_\phi = f_{O_2}^{\nu_{\phi\tilde{s}}} \prod_{s=1}^{\dot{s}} a_s^{\nu_{\phi s}}$$

Mass action for solid-solution end-member components ($\psi = 1,\acute{\psi}$; $\chi = 1,\hat{\chi}_\psi$)

$$K_{\chi\psi} = a_{\chi\psi}^{\nu_{\chi\psi\chi\psi}} f_{O_2}^{\nu_{\chi\psi\tilde{s}}} \prod_{s=1}^{\dot{s}} a_s^{\nu_{\chi\psi s}}$$

Activity-concentration relation for aqueous solute species ($s = 2,\hat{s}$)

$$a_s = m_s \gamma_s$$

Activity-mole fraction relation for solid-solution end-members ($\psi = 1,\hat{\psi}$; $\chi = 1,\hat{\chi}_\psi$)

$$a_{\chi\psi} = x_{\chi\psi} \lambda_{\chi\psi}$$

Definition of the equivalent stoichiometric ionic strength of a sodium chloride solution ($\epsilon^{\pm}$ = Na or Cl)

$$\tilde{I} = \sum_{s=2}^{\hat{s}} k_{\epsilon^{\pm} s} m_s$$

Table 1. Continued.

Definition of true ionic strength

$$I = \tfrac{1}{2}\sum_{s=2}^{\hat{s}} m_s z_s^2$$

Activity of liquid water[1]

$$\log a_w = -2/(2.303\omega)\,\tilde{I}\,\hat{\phi}$$

where $\hat{\phi} = 1 - DJ + b_2\tilde{I}/2 + 2b_3\tilde{I}^2/3 + 3b_4\tilde{I}^3/4$ (osmotic coefficient)

$$D = 2.303A/(b_1{}^3\tilde{I})$$

$$\hat{B} = 1 + b_1\sqrt{\tilde{I}}$$

$$J = \hat{B} - 2\ln\hat{B} - 1/\hat{B}$$

Activity coefficients of aqueous solutes ($s = 2,\hat{s}$)

$$\log \gamma_s = f_s(I)$$

where f_s is one of the functions listed in Table 2

Activity coefficients of solid-solution end-member components ($\psi = 1,\hat{\psi}$; $\chi = 1,\hat{\chi}_\psi$)

$$\log \lambda_{\chi=i,\psi} = g_{\chi\psi}(x_{\chi=j\neq i,\psi}, x_{\chi=k\neq i,\psi}, \ldots)$$

where $g_{\chi\psi}$ is one of the functions listed in Table 3

Molal concentrations of aqueous solutes ($s = 2, \hat{s}$)

$$m_s = \omega n_s/n_w$$

Mole fractions of solid-solution end-members ($\psi = 1,\hat{\psi}$; $\chi = 1,\hat{\chi}_\psi$)

$$x_{\chi=i,\psi} = n_{\chi=i,\psi} \Big/ \left(\sum_{\chi=1}^{\hat{\chi}_\psi} n_{\chi\psi}\right)$$

---

[1] Helgeson et al. (1970).

Table 2. Activity coefficient functions for aqueous solute species discussed by Helgeson (1968, 1969) and Helgeson et al. (1970).

Ideal behavior; suitable for slightly to moderately polar neutral species

$$\log \gamma_s = 0$$

Extended Debye-Huckel equation; suitable for charged species

$$\log \gamma_s = -Az_s^2\sqrt{I}/(1 + \mathring{a}_s B\sqrt{I}) + \dot{B}I$$

Power series fit to aqueous carbon dioxide data; suitable for dissolved gas species and other neutral, low polarity species

$$\log \gamma_s = c_1 I + c_2 I^2 + c_3 I^3 + c_4 I^4$$

Table 3. Some conventional models for treating solid solutions: excess free energy functions and activity coefficient relations.

Ideal solution

$$G_{xs} = 0$$

$$2.303\ RT \log \lambda_\chi = 0, \text{ all } \chi$$

Third-order Maclaurin, binary solution[1,2]

$$G_{xs} = W_1x_2 + W_2x_2^2/2! + W_3x_2^3/3!$$

$$2.303\ RT \log \lambda_1 = -W_2x_2^2/2 - W_3x_2^3/3$$

$$2.303\ RT \log \lambda_2 = (-W_2/2 - W_3/2)x_1^2 + W_3x_1^3/3 + (W_1 + W_2/2 + W_3/6)$$

Binary regular[3]

$$G_{xs} = Wx_1x_2$$

$$2.303\ RT \log \lambda_1 = Wx_2^2$$

$$2.303\ RT \log \lambda_2 = Wx_1^2$$

---

[1] Note that $\log \lambda_2 \rightarrow 0$ as $x_1 \rightarrow 0$ only if $(W_1 + W_2/2 + W_3/6) = 0$. If this condition is not satisfied, then this treatment should not be applied to phases which exhibit continuous solid solution. This treatment was incorrectly programmed in the original PATHI program described by Helgeson et al. (1970).

[2] Compare to Helgeson et al. (1970) and references therein.

[3] Compare to Saxena (1973, p.11-12).

Table 3. *Continued.*

Guggenheim polynomial, binary solution [4]

$$G_{xs} = x_1x_2\left[W_1 + W_2(x_1 - x_2) + W_3(x_1 - x_2)^2\right]$$

$$2.303\ RT \log \lambda_1 = (W_1 + 3W_2 + 5W_3)x_2^2 + (-4W_2 - 16W_3)x_2^3 + 12W_3x_2^4$$

$$2.303\ RT \log \lambda_2 = (W_1 - 3W_2 + 5W_3)x_1^2 + (4W_2 - 16W_3)x_1^3 + 12W_3x_1^4$$

Ternary regular[5]

$$G_{xs} = x_1^2(W_{13} + W_{12}) + x_2^2(W_{12} + W_{23}) + x_3^2(W_{13} + W_{23}) + x_1x_2(W_{13} - W_{12} + W_{23}) + x_2x_3(W_{12} - W_{23} + W_{13}) + x_1x_3(W_{23} - W_{13} + W_{12})$$

$$2.303\ RT \log \lambda_1 = W_{12}x_2^2 + W_{13}x_3^2 + x_2x_3(W_{12} - W_{23} + W_{13})$$

$$2.303\ RT \log \lambda_2 = W_{23}x_3^2 + W_{12}x_1^2 + x_1x_3(W_{12} - W_{13} + W_{23})$$

$$2.303\ RT \log \lambda_3 = W_{13}x_1^2 + W_{23}x_2^2 + x_1x_2(W_{13} - W_{12} + W_{23})$$

Cubic Maclaurin, binary solution[6]

$$G_{xs} = x_1x_2(W_1 x_2 + W_2x_1)$$

$$2.303\ RT \log \lambda_1 = (2W_2 - W_1)x_2^2 + 2(W_1 - W_2)x_2^3$$

$$2.303\ RT \log \lambda_2 = (2W_1 - W_2)x_1^2 + 2(W_2 - W_1)x_1^3$$

---

[4] Compare to Saxena (1973, p. 14-15).

[5] Compare to Prigogine and Defay (1954, p. 257).

[6] Compare to Saxena (1973, p. 16).

The set of equations in Tables 1-3 includes mass-balance, mass action, non-ideality, and definitional relations, and presents an equal number of unknowns, including masses, concentrations, mole-fractions, activities, activity coefficients, etc. For numerical facility it is desirable to reduce the number of unknowns by a sequence of substitutions involving the initial set of equations. I have chosen as operating variables the masses of a basis set of aqueous species, the oxygen fugacity, and the masses of mineral species present in the modelled system. Eliminating the masses of aqueous complexes and simple ions of alternate oxidation state required the adoption also of the ionic strength parameters $\tilde{I}$ and I as operating variables. This was necessary to avoid an infinite loop of substitutions in the mathematical derivations, to be presented. Because these quantities (masses, f_{O_2}, $\tilde{I}$, I) are all inherently non-negative functions, their logarithmic forms were adopted. This prevents physically unrealistic estimates from occurring during the iteration process (an old trick; cf. Van Zeggeren and Storey, 1970, p. 94). Thus, the vector $\underline{z}$ of operating variables has the general form

$$\underline{z} \equiv \begin{bmatrix} \ell_{w} \\ \ell_{s=2} \\ \vdots \\ \ell_{s=\dot{s}} \\ \log f_{O_2} \\ \log \tilde{I} \\ \log I \\ \ell_{\phi=1} \\ \vdots \\ \ell_{\phi=\hat{\phi}} \\ \ell_{\chi=1,\,\psi=1} \\ \vdots \\ \ell_{\chi=\hat{\chi}_{\psi},\psi=1} \\ \vdots \\ \ell_{\chi=1,\psi=\hat{\psi}} \\ \vdots \\ \ell_{\chi=\hat{\chi}_{\psi},\psi=\hat{\psi}} \end{bmatrix}$$

The corresponding set of reduced equations is given in Table 4.

Table 4. A reduced set of equations in logarithmic unknowns for describing a chemical equilibrium problem.

Modified mass balances ($\epsilon = 1,\hat{\epsilon}$)

$$0 = -n_{\epsilon}^{t} + \sum_{s=1}^{\dot{s}} k_{\epsilon s} 10^{\ell_s} + \sum_{r=1}^{\hat{r}} k_{\epsilon s*} 10^{\ell_{s*}} + \sum_{\phi=1}^{\hat{\phi}} k_{\epsilon\phi} 10^{\ell_{\phi}} + \sum_{\psi=1}^{\hat{\psi}} \sum_{\chi=1}^{\hat{\chi}_{\psi}} k_{\epsilon\chi\psi} 10^{\ell_{\chi\psi}}$$

$$\text{where } \ell_{s*} = \Bigg[\log K_r - \nu_{rw} \log a_w - \nu_{r\tilde{s}} \log f_{O_2} - \nu_{rs*} \log \gamma_{s*} - \nu_r^{t}(\log \omega - \ell_w) - \sum_{s=2}^{\dot{s}} \nu_{rs} (\ell_s + \log \gamma_s) \Bigg] / \nu_{rs*}$$

$$\text{and } \nu_r^{t} = \left(\nu_{rs*} + \sum_{s=2}^{\dot{s}} \nu_{rs} \right)$$

and $\log \gamma_s$ and $\log \lambda_{\chi\psi}$ are replaced in all equations by appropriate expressions from Tables 2 and 3, respectively.

Table 4. Continued.

Modified charge balance

$$0 = \sum_{s=2}^{\dot{s}} z_s 10^{\ell_s} + \sum_{r=1}^{\hat{r}} z_{s*} 10^{\ell_{s*}}$$

Equivalent stoichiometric ionic strength

$$0 = -\log \tilde{I} + \log \left(\sum_{s=2}^{\dot{s}} \nu_{\epsilon^{\pm}s} \omega 10^{(\ell_s - \ell_w)} + \sum_{r=1}^{\hat{r}} \nu_{\epsilon^{\pm}s*} \omega 10^{(\ell_{s*} - \ell_w)} \right)$$

True ionic strength

$$0 = -\log I + \log \left(½ \sum_{s=2}^{\dot{s}} z_s^2 \omega 10^{(\ell_s - \ell_w)} + ½ \sum_{r=1}^{\hat{r}} z_{s*}^2 \omega 10^{(\ell_{s*} - \ell_w)} \right)$$

Mass action for a pure mineral ($\phi = 1,\hat{\phi}$)

$$0 = -\log K_\phi + \nu_{\phi w} \log a_w + \nu_{\phi\tilde{s}} \log f_{O_2} + \nu_\phi^t (\log \omega - \ell_w) + \sum_{s=2}^{\dot{s}} \nu_{\phi s} (\ell_s + \log \gamma_s)$$

$$\text{where } \nu_\phi^t = \sum_{s=2}^{\dot{s}} \nu_{\phi s}$$

Mass action for a solid-solution end-member component ($\psi = 1,\hat{\psi}$; $\chi = 1,\hat{\chi}_\psi$)

$$0 = -\log K_{\chi\psi} + \nu_{\chi\psi w} \log a_w + \nu_{\chi\psi\tilde{s}} \log f_{O_2} + \nu_{\chi\psi}^t (\log \omega - \ell_w) + \nu_{\chi\psi\chi\psi} (\log x_{\chi\psi} + \log \lambda_{\chi\psi})$$
$$+ \sum_{s=2}^{\dot{s}} \nu_{\chi\psi s} (\ell_s + \log \gamma_s)$$

$$\text{where } \nu_{\chi\psi}^t = \sum_{s=2}^{\dot{s}} \nu_{\chi\psi s}$$

These equations may be solved simultaneously by the Newton-Raphson method (cf. Van Zeggeren and Storey, 1970, Sec. 4.2.2, p. 92-94; Sec. 5.2.3, p. 137-139). Given an estimate for the vector $\underline{z}$ of operating variables, the error can be measured by the residual vector $\underline{\alpha}$, whose elements correspond to the right-hand-sides of the equations of Table 4. The Newton-Raphson method is applied by computing a correction vector $\underline{\delta}$ from the equation

$$\underline{\underline{J}}\underline{\delta} = -\underline{\alpha} \tag{1}$$

where $\underline{\underline{J}}$ is the Jacobian matrix $(\partial \alpha_i/\partial z_j)$ whose elements are presented in Tables 5-7. A new estimate of $\underline{z}$ is then computed by

$$\underline{z}_{i+1} = \underline{z}_i + \underline{\delta}_i . \tag{2}$$

In addition to $\underline{\alpha}$, other useful residual functions may be defined:

$\underline{\beta}$, identical to $\underline{\alpha}$ except that $\beta_\epsilon = \alpha/n_\epsilon^t$, $\epsilon = 1,\hat{\epsilon}$;
β_{max}, the largest magnitude of any element of $\underline{\beta}$; and
β_{rms}, the root-mean-square of the elements of $\underline{\beta}$.

Note that $\underline{\alpha}$, $\underline{\beta}$, β_{max}, β_{rms}, $\underline{\delta}$, and δ_{max} (analogous to β_{max}) all approach zero as the iteration converges. Program EQ6 tests for convergence by comparing each of β_{max} and δ_{max} with a user-specified tolerance parameter (usually in the range 10^{-6} to 10^{-10}). It is also useful to define a convergence function:

$$\beta_{conv,i} = (\beta_{max,i-1} - \beta_{max,i})/\beta_{max,i-1}.$$

Note that this function is negative if the iteration is diverging, close to zero if little improvement is being made, and approaches unity if the iteration is converging rapidly. The function δ_{conv} is analogous to β_{conv} and has the same properties.

Table 5. Elements of the Jacobian matrix ($\underline{\underline{J}}$).[1]

$$\partial\alpha_\epsilon/\partial\ell_w = 2.303k_{\epsilon w}10^{\ell_w} + \sum_{r=1}^{\hat{r}} 2.303k_{\epsilon s^*}\nu_r^t 10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_\epsilon/\partial\ell_{s\neq w} = 2.303k_{\epsilon s}10^{\ell_s} + \sum_{r=1}^{\hat{r}} 2.303k_{\epsilon s^*}\nu_{rs}10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_\epsilon/\partial \log f_{O_2} = -\sum_{r=1}^{\hat{r}} 2.303k_{\epsilon s^*}\nu_{r\tilde{s}}10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_\epsilon/\partial \log \tilde{I} = -\sum_{r=1}^{\hat{r}} 2.303k_{\epsilon s^*}\nu_{rw}C_w 10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_\epsilon/\partial \log I = -\sum_{r=1}^{\hat{r}} 2.303k_{\epsilon s^*}\left(\nu_{rs^*}C_{s^*} + \sum_{s=2}^{\dot{s}} \nu_{rs}C_s\right) 10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_\epsilon/\partial\ell_\phi = 2.303k_{\epsilon\phi}10^{\ell_\phi}$$

$$\partial\alpha_\epsilon/\partial\ell_{\chi\psi} = 2.303k_{\epsilon\chi\psi}\,10^{\ell_{\chi\psi}}$$

$$\partial\alpha_z/\partial\ell_w = \sum_{r=1}^{\hat{r}} 2.303z_{s^*}\nu_r^t 10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_z/\partial\ell_{s\neq w} = 2.303z_s10^{\ell_s} - \sum_{r=1}^{\hat{r}} 2.303z_{s^*}\,\nu_{rs}10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_z/\partial \log f_{O_2} = -\sum_{r=1}^{\hat{r}} 2.303z_{s^*}\nu_{r\tilde{s}}\,10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_z/\partial \log \tilde{I} = -\sum_{r=1}^{\hat{r}} 2.303z_{s^*}\,\nu_{rw}C_w 10^{\ell_{s^*}}/\nu_{rs^*}$$

$$\partial\alpha_z/\partial \log I = -\sum_{r=1}^{\hat{r}} 2.303z_{s^*}\left(\nu_{rs^*}C_{s^*} + \sum_{s=2}^{\dot{s}} \nu_{rs}C_s\right) 10^{\ell_{s^*}}$$

$$\partial\alpha_z/\partial\ell_\phi = 0$$

$$\partial\alpha_z/\partial\ell_{\chi\psi} = 0$$

Table 5. Continued.

$$\partial \alpha_{\widetilde{I}}/\partial \ell_w = \left(\omega 10^{-\ell_w}/\widetilde{I}_{calc}\right)\left(-\sum_{s=2}^{\dot{s}} k_{\epsilon \pm_s} 10^{\ell_s} + \sum_{r=1}^{\hat{r}} k_{\epsilon \pm_{s*}} \left[\left(\nu_r^t/\nu_{rs*}\right) - 1\right] 10^{\ell_{s*}}\right)$$

$$\partial \alpha_{\widetilde{I}}/\partial \ell_{s \neq w} = \left(\omega 10^{-\ell_w}/\widetilde{I}_{calc}\right)\left(k_{\epsilon \pm_s} 10^{\ell_s} - \sum_{r=1}^{\hat{r}} k_{\epsilon \pm_{s*}} \nu_{rs} 10^{\ell_{s*}}/\nu_{rs*}\right)$$

$$\partial \alpha_{\widetilde{I}}/\partial \log f_{O_2} = \left(\omega 10^{-\ell_w}/\widetilde{I}_{calc}\right)\left(-\sum_{r=1}^{\hat{r}} k_{\epsilon \pm_{s*}} \nu_{r\tilde{s}} 10^{\ell_{s*}}/\nu_{rs*}\right)$$

$$\partial \alpha_{\widetilde{I}}/\partial \log \widetilde{I} = \left(\omega 10^{-\ell_w}/\widetilde{I}_{calc}\right)\left(-\sum_{r=1}^{\hat{r}} k_{\epsilon \pm_{s*}} \nu_{rw} C_w 10^{\ell_{s*}}/\nu_{rs*}\right) - 1$$

$$\partial \alpha_{\widetilde{I}}/\partial \log I = \left(\omega 10^{-\ell_w}/\widetilde{I}_{calc}\right)\left[-\sum_{r=1}^{\hat{r}} k_{\epsilon \pm_{s*}} \left(\sum_{s=2}^{\dot{s}} \nu_{rs} C_s/\nu_{rs*} + C_{s*}\right) 10^{\ell_{s*}}\right]$$

$$\partial \alpha_{\widetilde{I}}/\partial \ell_{\phi} = 0$$

$$\partial \alpha_{\widetilde{I}}/\partial \ell_{\chi\psi} = 0$$

$$\partial \alpha_{I}/\partial \ell_w = \left(\omega 10^{-\ell_w}/2I_{calc}\right)\left(-\sum_{s=2}^{\dot{s}} z_s^2 10^{\ell_s} + \sum_{r=1}^{\hat{r}} z_{s*}^2 \left[\left(\nu_r^t/\nu_{rs*}\right) - 1\right] 10^{\ell_{s*}}\right)$$

$$\partial \alpha_{I}/\partial \ell_{s \neq w} = \left(\omega 10^{-\ell_w}/2I_{calc}\right)\left(z_s^2 10^{\ell_s} - \sum_{r=1}^{\hat{r}} z_{s*}^2 \nu_{rs} 10^{\ell_{s*}}/\nu_{rs*}\right)$$

$$\partial \alpha_{I}/\partial \log f_{O_2} = \left(\omega 10^{-\ell_w}/2I_{calc}\right)\left(-\sum_{r=1}^{\hat{r}} z_{s*}^2 \nu_{r\tilde{s}} 10^{\ell_{s*}}/\nu_{rs*}\right)$$

$$\partial \alpha_{I}/\partial \log \widetilde{I} = \left(\omega 10^{-\ell_w}/2I_{calc}\right)\left(-\sum_{r=1}^{\hat{r}} z_{s*}^2 \nu_{rw} C_w 10^{\ell_{s*}}/\nu_{rs*}\right)$$

$$\partial \alpha_{I}/\partial \log I = \left(\omega 10^{-\ell_w}/2I_{calc}\right)\left[-\sum_{r=1}^{\hat{r}} z_{s*}^2 \left(\sum_{s=2}^{\dot{s}} \nu_{rs} C_s/\nu_{rs*} + C_{s*}\right) 10^{\ell_{s*}}\right] - 1$$

$$\partial \alpha_{I}/\partial \ell_{\phi} = 0$$

$$\partial \alpha_{I}/\partial \ell_{\chi\psi} = 0$$

$$\partial \alpha_{\phi}/\partial \ell_w = -\nu_{\phi}^t$$

$$\partial \alpha_{\phi}/\partial \ell_{s \neq w} = \nu_{\phi s}$$

$$\partial \alpha_{\phi}/\partial \log f_{O_2} = \nu_{\phi\tilde{s}}$$

Table 5. Continued.

$$\partial\alpha_{\phi}/\partial \log \tilde{I} = \nu_{\phi w} C_w$$

$$\partial\alpha_{\phi}/\partial \log I = \sum_{s=2}^{\dot{s}} \nu_{\phi s} C_s$$

$$\partial\alpha_{\phi}/\ell_{\phi} = 0$$

$$\partial\alpha_{\phi}/\partial\ell_{\chi\psi} = 0$$

$$\partial\alpha_{\chi\psi}/\partial\ell_{w} = -\nu_{\chi\psi}{}^{t}$$

$$\partial\alpha_{\chi\psi}/\partial\ell_{s\neq w} = \nu_{\chi\psi s}$$

$$\partial\alpha_{\chi\psi}/\partial \log f_{O_2} = \nu_{\chi\psi\tilde{s}}$$

$$\partial\alpha_{\chi\psi}/\partial \log \tilde{I} = \nu_{\chi\psi w}\ C_w$$

$$\partial\alpha_{\chi\psi}/\partial \log I = \sum_{s=2}^{\dot{s}} \nu_{\chi\psi s}\ C_s$$

$$\partial\alpha_{\chi\psi}/\partial\ell_{\phi} = 0$$

$$\partial\alpha_{\chi,\psi=i}/\partial\ell_{\chi,\psi=j} = 0$$

$$\partial\alpha_{\chi=i,\psi}/\partial\ell_{\chi=i,\psi} = \nu_{\chi\psi\chi\psi} \left[(1 - x_{\chi=i,\psi}) - \sum_{\substack{\chi=j \\ \chi\neq i}} S_{\chi=i,\chi=j,\psi}\, x_{\chi=j,\psi} \right]$$

$$\partial\alpha_{\chi=i,\psi}/\partial\ell_{\chi=j,\psi} = \nu_{\chi\psi\chi\psi} \left[-x_{\chi=j,\psi} + S_{\chi=i,\chi=j,\psi}(1 - x_{\chi=j,\psi}) - \sum_{\substack{\chi=k \\ \chi\neq j \\ \chi\neq i}} S_{\chi=i,\chi=k,\psi}\, x_{\chi=j,\psi} \right]$$

---

[1] Expressions for C and S functions are defined in Tables 6 and 7, respectively. The parameters $\tilde{I}_{calc}$ and I_{calc} are defined in Table 1, and ℓ_{s*} in Table 4.

Table 6. C_s functions for aqueous species.[1] These equations correspond to those in Tables 1 and 2.

Water (Table 1)

$$C_w = -(2/2.303\omega)\left[\hat{\phi} + JD - (Db_1{}^3\tilde{I}^{3/2}/2B^2) + (b_2\,\tilde{I}\,/2) + (4b_3\,\tilde{I}^2/3) + (9b_4\,\tilde{I}^3/4)\right]$$

Ideal behavior (Table 2)

$$C_s = 0$$

Extended Debye-Huckel equation (Table 2)

$$C_s = -Az_s{}^2 I^{-1/2}/\left[2(1 + \mathring{a}_s B I^{1/2})^2\right] + \dot{B}$$

Power series (Table 2)

$$C_s = c_1 + 2c_2 I + 3c_3 I^2 + 4c_4 I^3$$

---

[1] Note that $C_w \equiv \partial \log a_w/\partial\tilde{I}$ and that $C_{s\neq w} \equiv \partial \log \gamma_s/\partial I$.

Table 7. **$S_{\chi=i,\chi=j,\psi}$ functions for solid-solution end-member components.**[1]

Ideal solution

$$S_{ij} = 0 \text{ for all } i,j$$

Third-order Maclaurin, binary solution

$$S_{12} = (-W_2 x_2^2 - W_3 x_2^3)/RT$$

$$S_{21} = \left[-(W_1 + W_3)x_1^2 + W_3 x_1^3\right]/RT$$

Binary regular solution

$$S_{12} = (2W x_2^2)/RT$$

$$S_{21} = (2W x_1^2)/RT$$

Guggenheim polynomial, binary solution

$$S_{12} = \left[2(W_1 + 3W_2 + 5W_3)x_2^2 + 3(-4W_2 - 16W_3)x_2^3 + 48W_3 x_2^4\right]/RT$$

$$S_{21} = \left[2(W_1 - 3W_2 + 5W_3)x_1^2 + 3(4W_2 - 16W_3)x_1^3 + 48W_3\, x_1^4\right]/RT$$

Ternary regular solution

$$S_{12} = \left[2W_{12}x_2^2 + (W_{12} - W_{23} + W_{13})x_3 x_2\right]/RT$$

$$S_{13} = \left[2W_{13}x_3^2 + (W_{12} - W_{23} + W_{13})x_2 x_3\right]/RT$$

$$S_{21} = \left[2W_{12}x_1^2 + (W_{12} - W_{13} + W_{23})x_3 x_1\right]/RT$$

$$S_{23} = \left[2W_{23}x_3^2 + (W_{12} - W_{13} + W_{23})x_1 x_3\right]/RT$$

$$S_{31} = \left[2W_{13}x_1^2 + (W_{13} - W_{12} + W_{23})x_2 x_1\right]/RT$$

$$S_{32} = \left[2W_{23}x_2^2 + (W_{13} - W_{12} + W_{23})x_1 x_2\right]/RT$$

Cubic Maclaurin, binary solution

$$S_{12} = \left[2(2W_2 - W_1)x_2^2 + 6(W_1 - W_2)x_2^3\right]/RT$$

$$S_{21} = \left[2(2W_1 - W_2)x_1^2 + 6(W_2 - W_1)x_1^3\right]/RT$$

---

[1] Note that $S_{ij} \equiv \partial \log \lambda_i / \partial \log x_j$, is a purely formal partial derivative of the expressions in Table 3, and is not any form of partial molal quantity, such as a chemical potential.

Several problems remain. Newton-Raphson iteration, when it converges, is usually sufficiently fast. Unfortunately, however, the basic method outlined thus far may diverge. In particular, the Jacobian matrix ($\underline{\underline{J}}$) may become singular or so ill-conditioned with respect to machine word length that the correction vector $\underline{\delta}$ cannot be computed. Also, it has thus far been assumed that the mineral phase assemblage is known in advance. Special techniques and modifications to the Newton-Raphson method are required to treat these problems. Some are specific to the chemical equilibrium calculation dealt with here; others are very general.

UNDER-RELAXATION TECHNIQUES

A widely used device to enhance the probability of convergence is to replace Eq. (2) by

$$\underline{z}_{i+1} = \underline{z}_i + \kappa\,\underline{\delta}_i \quad , \tag{3}$$

where κ is a relaxation parameter (sometimes called a "convergence forcer," although it does not guarantee convergence) whose value lies on the interval (0,1]. It is especially useful when dealing with poor starting estimates. If the iteration is converging satisfactorily (as measured by $\beta_{\mathrm{conv}} \simeq \kappa$), then under-relaxation should be discontinued ($\kappa = 1$).

Several schemes can be adopted to manage κ. The simplest device is to choose a constant value of ¼ or ½ until five to ten iterations have been done or until β_{conv} (or δ_{conv}) shows that convergence is proceeding satisfactorily.

A second device is to place a limit δ' on the magnitude of the Newton-Raphson correction on any iteration. If $\delta_{\max} > \underline{\delta}'$, where δ' might have a value of, say, 2.0, then choose

$$\kappa = \delta'/\delta_{\max} \quad . \tag{4}$$

This scheme keeps the iteration from blowing up (via overflow during the arithmetic of computing the new residual functions or new Jacobian) by very large elements of $\underline{\delta}$ in a single iteration.

A third technique is to incrementally reduce κ to decrease an absolute measure of divergence, $(\beta_{\max,i+1} - \beta_{\max,i}) > 0$, to within some chosen tolerance. If the number of incremental attempts becomes large, it is likely that convergence cannot be induced, and the iteration should be terminated in favor of pursuing some other course of action (such as changing the mineral phase assemblage).

All three of these strategies have been incorporated into program EQ6. Extensive testing has found them necessary and satisfactory. A fourth scheme, not used in EQ6, is to locate the optimal value of κ on each iteration. A suitable single-valued residual function that is a continuous function of κ (such as β_{rms}) is minimized on the interval (0,1]. Such methods have been discussed in detail by Ting-Po and Nancollas (1972).

OPTIMIZING STARTING ESTIMATES

During development of program EQ6 it was found that, if an element mass balance residual were more than slightly negative at the start of iteration, it would become increasingly negative instead of improving and the iteration would diverge. For $\beta_\epsilon \gtrsim -0.1$ (10% mass deficiency) very little risk of this was observed; but for $\beta_\epsilon \lesssim -0.5$ (50% mass deficiency) it occurred frequently. The problem was usually associated with a minor element, such as Cu, and could be avoided by incrementing the corresponding basis aqueous species variable (e.g., $\ell_{\mathrm{Cu}^{++}}$) prior to Newton-Raphson iteration until the mass balance residual became non-negative. This simple, fast procedure eliminates the need for a time-consuming, curve-crawling technique proposed by Crerar (1975). That method requires first solving with only the major elements present, then calculating the numerical equivalents of steps on a reaction path to place the minor metals into the system.

The above observation suggests a parallel approach for choosing starting estimates for the logarithmic masses (ℓ) of solids added to the phase assemblage. The mass of any new phase is physically limited by the masses of its constituent elements present in the system. Choice of a starting estimate comparable to this limit insures positive starting mass balance residuals; this yielded excellent results during testing, even when some of the mass balance residuals were highly positive ($\beta_\epsilon \approx 1.0$, 100% calculated mass excess).

FINDING THE CORRECT PHASE ASSEMBLAGE

The method described so far requires that the mineral assemblage be specified *a priori*. However, often it is not known in advance, and may be difficult to guess. By successively modifying a sequence of assumed, provisional phase assemblages it is possible to find one that satisfies all the governing equations.

First one should ask, how many mathematical solutions may exist? The phase assemblage may not be unique (i.e., more than one may occur) if the temperature and pressure fall on an invariant point or a univariant curve of some mineral assemblage. For example, if the chosen temperature and pressure lie on the univariant curve of two polymorphs

A and B, then three "correct" phase assemblages could occur: aqueous solution-A, aqueous solution-B, and aqueous solution-A-B. The last assemblage could not be computed by the iteration procedure described here because the rows in the Jacobian matrix for the mass action expressions for A and B would be identical, causing a singularity. With these considerations in mind, I shall take the first "correct" assemblage successfully computed as the only correct assemblage.

I shall assume that, once a satisfactory phase assemblage has been found, no further question of uniqueness need be considered. This is perhaps an article of faith—believing that the Gibbs free energy function is truly convex. Studies by applied mathematicians have shown that this indeed holds for thermodynamically ideal systems (Hancock and Motzkin, 1960; Shapiro and Shapley, 1965). However, it has been demonstrated (Caram and Scriven, 1976; Othmer, 1976) that it may not be true when some popular non-ideality relations are applied (e.g., the regular solution model in Table 3).

The phase selection scheme adopted involves modifying the provisional assemblage by adding one phase, deleting one phase, or (occasionally) replacing one phase by another. This one-at-a-time restriction, adopted also by Morel and Morgan (1972), serves two purposes. First, the selection process may occasionally make a wrong choice, such as deleting a phase which should actually be present. Restricting the number of simultaneous changes in the assumed assemblage facilitates recovery from such an error. Second, more than a few phases may need to be added, as when eliminating supersaturations from a starting solution model created by program EQ3. If all possible phases were added at once, the burden on the Newton-Raphson iteration would be greatly increased. Also, the Jacobian matrix might be rendered singular by linear dependence among the rows corresponding to the solid species' mass action relationships. This occurs in formal violations of the Gibbs phase rule and also in cases in which the phase rule is satisfied only because the temperature and pressure happen to lie on an invariant point or univariant curve.

The Newton-Raphson iteration may converge or diverge for a given provisional phase assemblage. If it converges and one or more supersaturations remain, the supersaturated phases may be ranked according to decreasing affinity to precipitate. The affinity function of the j-th phase may be calculated as

$$A_j = 2.303\ RT(\log Q_j - \log K_j) \quad , \qquad (5)$$

where Q_j is the activity product of the phase (Helgeson, 1979). (For solid solution components, the calculation is not straightforward because Q_j depends on the assumed composition of the solid solution phase; see Helgeson *et al.*, 1970.) The phase with the highest affinity may then be added to the provisional assemblage (Morel and Morgan, 1972). (To avoid a possible conflict between the addition and deletion mechanisms, no phase should be added to the system unless its affinity exceeds some small tolerance.)

Two problems may occur when the above scheme is used. First, affinities (also log Q and log K) are dependent on molecular formulas and reaction coefficients, both of which are arbitrary. Consider the dissolution of calcite:

$$CaCO_{3\,(calcite)} \rightleftarrows Ca^{++} + CO_3^{=} \quad .$$

Doubling the molecular formula,

$$Ca_2(CO_3)_2 \rightleftarrows 2\ Ca^{++} + 2\ CO_3^{=} \quad ,$$

or doubling the reaction coefficients,

$$2\ CaCO_3 \rightleftarrows 2\ Ca^{++} + 2\ CO_3^{=} \quad ,$$

doubles log Q, log K, and the affinity. Choosing a new phase on the basis of chemical affinities therefore has a built-in bias in favor of phases with large molecular formulas, such as clay minerals. The affinities may instead be scaled by dividing by a factor which takes into account the number of aqueous species participating in the dissolution or precipitation of the phase:

$$\nu_{j,\text{scale}} \equiv \sum_{s=1}^{\tilde{s}} \left| \nu_{js} \right| \quad . \qquad (6)$$

A second problem when several new phases must be added is that a highly insoluble phase, such as hematite, may have a very high affinity even though the maximum mass that may be precipitated is very small. If such a phase is among the first to be added, its presence in the Jacobian will tend to hold its calculated activity product close to the equilibrium value and ''anchor'' the corresponding aqueous basis species (including H^+, in the case of hematite). This can greatly decrease the rate of convergence, or even lead to divergence, when a major precipitate is added to the assemblage later. The problem can be eliminated by first examining the maximum precipitable mass of each phase, i.e., the limit imposed by the masses of the component elements in the aqueous phase. If this is very small, the scaled affinity of the phase may be arbitrarily reduced. (This has been tested by reducing the scaled affinity of a phase by a factor of 100 whenever its maximum precipitable mass is less than 10^{-6} mole.) This causes highly insoluble trace phases to be placed in the phase assemblage *after* the major precipitates have been added.

This method of computing scaled affinities to choose a phase to add to the mineral assemblage is a distinct improvement over directly using chemical affinities. Other techniques for scaling might be adopted; the ones chosen here are admittedly empirical. Their justification is that they have produced good results.

The Newton-Raphson iteration procedure fails to converge, obviously, if no mathematical solution exists for the assumed set of mineral phases. It might, of course, diverge for other reasons, such as a bad set of starting estimates. Experience with EQ6 has shown that the techniques of optimizing starting estimates and of under-relaxation so improve the method that divergence is a reliable indication that a phase assumed to be present should be dropped. The single exception to this generalization is that divergence is also sometimes caused by a poor starting estimate for the oxygen fugacity. As will be shown later, this condition is easily detected.

Divergence caused by an inappropriate mineral assemblage may be divided into two cases. First, the Jacobian matrix may be singular at the start because of an apparent phase rule violation. In this case, a subset of the mineral mass-action rows exhibits linear dependence. Second, iteration may proceed one or more steps before ceasing (the matrix may become too ill-conditioned to solve or iteration may be terminated by programmed criteria). Other workers (e.g., Morel and Morgan, 1972; Bos and Meershoek, 1972; others cited by Van Zeggeren and Storey, 1970, p. 141-144) have deleted solids for which negative masses are calculated. However, such physically unrealistic mathematical solutions cannot be obtained by the method described in this report because it uses logarithmic forms for all mass variables. Other techniques for choosing a phase for deletion must therefore be found.

Let us first consider the case of an apparent phase rule violation. This can occur only on adding a new mineral to the system. The subset of minerals involved can be found by testing for linear dependence. A mineral is involved if the set of mass action rows corresponding only to the other minerals in the provisional assemblage is linearly independent. An affinity-based criterion can then be used to choose which mineral in this subset should be deleted.

For each mineral in the subset, one may calculate its hypothetical affinity in the presence of others. Suppose the subset consists of quartz (SiO_2), periclase (MgO), and enstatite ($MgSiO_3$). The dissolution reactions and their respective conditions for chemical equilibrium are:

$$\text{quartz} \rightleftarrows SiO_2^{\circ}$$

$$Q_{\text{quartz}} \equiv \log a_{SiO_2^{\circ}} = \log K_{\text{quartz}} \tag{7}$$

$$\text{periclase} + 2\,H^+ \rightleftarrows Mg^{++} + H_2O_{(\ell)}$$

$$Q_{\text{periclase}} \equiv \log a_{Mg^{++}} + \log a_{H_2O_{(\ell)}} - 2 \log a_{H^+} = \log K_{\text{periclase}} \tag{8}$$

$$\text{enstatite} + 2\,H^+ \rightleftarrows Mg^{++} + H_2O_{(\ell)} + SiO_2^{\circ}$$

$$Q_{\text{enstatite}} \equiv \log a_{Mg^{++}} + \log a_{H_2O_{(\ell)}} + \log a_{SiO_2^{\circ}} - 2 \log a_{H^+} = \log K_{\text{enstatite}} \quad . \tag{9}$$

In the presence of quartz and periclase,

$$\log Q_{\text{enstatite}} = \log K_{\text{quartz}} + \log K_{\text{periclase}} \quad . \tag{10}$$

Hence, the hypothetical affinity of enstatite is

$$A_{\text{enstatite}} = 2.303\ RT\ (\log K_{\text{quartz}} + \log K_{\text{periclase}} - \log K_{\text{enstatite}}) \quad . \tag{11}$$

Similarly,

$$A_{\text{quartz}} = 2.303\ RT\ (\log K_{\text{enstatite}} - \log K_{\text{periclase}} - \log K_{\text{quartz}}) \tag{12}$$

and

$$A_{\text{periclase}} = 2.303\ RT\ (\log K_{\text{enstatite}} - \log K_{\text{quartz}} - \log K_{\text{periclase}}) \quad . \tag{13}$$

Note that

$$A_{\text{periclase}} = A_{\text{quartz}} = -\ A_{\text{enstatite}} \quad . \tag{14}$$

If quartz or periclase were the last phase added, then

$$A_{\text{periclase}} = A_{\text{quartz}} > 0 > A_{\text{enstatite}} \quad . \tag{15}$$

This would indicate that only removal of enstatite from the system could lead to a system not supersaturated with respect to the other two solids. If, on the other hand, enstatite were the last phase added, then

$$A_{\text{periclase}} = A_{\text{quartz}} < 0 < A_{\text{enstatite}} \tag{16}$$

and the solid chosen to be deleted must be periclase or quartz. The logical procedure, in general, would be to choose the phase with the most negative hypothetical affinity. Here, however, the two negative affinities are equal. Testing of program EQ6 has shown that the procedure can be improved by scaling the hypothetical affinities in the manner used to choose a phase to add to the system. For the example above, this would indicate deletion of quartz. If a tie exists after scaling, one must make an arbitrary choice, such as deleting the phase with the lowest numerical index.

If divergence occurs after one or more iterations, or if the matrix is singular at the start but the mineral mass-action rows are linearly independent, four independent criteria may be applied to choose a phase for deletion. These criteria are based on empirical grounds, but have yielded good results during extensive testing of EQ6. Each criterion yields a value of a "decision" function for every solid in the assumed phase assemblage. The phase with the most negative value is the choice of the individual criterion. If no mineral has a negative-valued decision function, then the criterion produces no candidate for deletion. Of the maximum possible four candidates, the one with the most negative decision function is the deleted solid. Table 8 gives definitions of the four criteria adopted in EQ6. Other variations and specifications are possible; these have given good results.

Frequently, the logarithmic mass variable (see Table 8) of a mineral species that should not be present diverges toward minus infinity. This criterion is analogous to the convergence to a negative mass value discussed earlier. The decision function may be based on the final iterated value of the logarithmic mass variable, the value of the last correction term, or the value of the sum of the correction terms for all iteration steps. In these cases, the magnitude of the last correction term generated nearly always matches the under-relaxation limit δ' of Eq. (4). This is also how one can detect a poor starting estimate for oxygen fugacity (when $\delta_{\xi} = \delta'$).

A second device, applicable only when computing a reaction path, is to look for a phase whose mass is rapidly decreasing with reaction progress (ξ). The decision function is simply the derivative estimated from finite differences. This criterion almost always chooses the same candidate as the first. These two criteria generally produce decision functions which are much greater in magnitude than the other two, and are termed the *strong* criteria. They nearly always determine the dropped phase.

The last two criteria in Table 8, the *weak* criteria, are useful mainly very close to real or hypothetical phase boundaries; i.e., when a slight change in the elemental composition of the system would cause non-occurring phases to actually be present. In such a case, the logarithmic mass variable may fail to decrease, and the finite-difference Taylor's series, if available, may not predict sufficiently rapid drop in the mass of the phase. The third criterion is based on the fact that residual function elements β_{ϕ} and $\beta_{\chi\psi}$ are numerical analogs of dimensionless affinities ($\log Q_j - \log K_j$) for the respective mineral species. Negative values are analogous to the physical state of undersaturation, and can be used to choose the phase to be deleted. The fourth decision method is to search for a contrast between the mass balance residuals of elements that make up a phase and of those that do not. If the former are appreciably greater in magnitude than the latter, the phase is a candidate for deletion.

If the phase selection scheme fails to find the correct assemblage, some options remain. If a reaction path is being computed and is beyond the initial value of reaction progress, then the step size can be cut until the method works.

Table 8. Decision functions (Δ) for evaluating the j-th phase as a candidate for deletion from the provisional phase assemblage.

Logarithmic mass variable criterion

If one or more iterations were performed:

$$\Delta_1 \equiv \min \left\{ \ell_{j,\mathrm{final}} - \ell_{j,\mathrm{initial}}, 0 \right\}$$

If no iterations were performed:

$$\Delta_1 \equiv \min\left\{ \ell_j + 10, 0 \right\}$$

Derivative criterion (applicable only when computing a reaction path)

$$\Delta_2 \equiv \partial \ell_j/\partial \xi \text{ if } \partial \ell_j/\partial \xi < -200, \text{ else } \Delta_2 \equiv 0$$

Numerical undersaturation criterion

$$\Delta_3 \equiv \beta_j \text{ if } \beta_j < -10 \times (\text{tolerance on } \beta_{\max}), \text{ else } \Delta_3 \equiv 0$$

Mass residual contrast criterion

$$\Delta_4 \equiv \log \tilde{\beta}_{\mathrm{rms}} - \log \dot{\beta}_{\mathrm{rms}} \text{ if } \log \tilde{\beta}_{\mathrm{rms}} - \log \dot{\beta}_{\mathrm{rms}} < -1, \text{ else } \Delta_4 \equiv 0$$

$$\text{where } \tilde{\beta}_{\mathrm{rms}} \equiv \left[\left(\sum_{\tilde{\epsilon}} \beta_{\tilde{\epsilon}}^2 \right) / \tilde{j} \right]^{1/2}$$

where $\tilde{\epsilon}$ denotes an element that does not make up the phase, and $\tilde{j}$ is the number of such elements in the system

$$\dot{\beta}_{\mathrm{rms}} \equiv \left[\left(\sum_{\dot{\epsilon}} \beta_{\dot{\epsilon}}^2 \right) / \hat{j} \right]^{1/2}$$

where $\dot{\epsilon}$ denotes an element that makes up the phase, and $\hat{j}$ is the number of such elements

Otherwise, the user may select his own provisional phase assemblage and try again, or use reaction path techniques to find the right assemblage. As an example of the latter, suppose a starting aqueous solution exhibits several supersaturations and the phase selection method fails. The user may then suppress all phases (by ignoring supersaturations) and titrate in some component such as HCl (or H_2 or O_2 if the phase problem is mainly a redox one) until all affinities indicate no supersaturations, or some so few and small that the phase selection scheme will now work. Phase suppression may then be lifted and the components that were titrated in may be titrated out, until the desired system is found.

COMPUTING REACTION PATH MODELS

TYPES OF MODELS

The Newton-Raphson procedure described here may now be applied to the calculation of partial equilibrium reaction path models of mass transfer, which have been discussed by Helgeson (1968, 1979). Tracing a reaction path involves, in its simplest form, changing the mass constraints (n_ϵ^t, $\epsilon = 1, \hat{\epsilon}$) on the closed system $\tilde{E}$ (the equilibrium subsystem) so that a series of compositionally neighboring chemical equilibrium problems may be solved. The user specifies a set of $\hat{\rho}$ reactants ($\hat{\rho}$ may be zero) and a corresponding set of reactant tracking coefficients (ξ), which may be interpreted as relative rate constants (Helgeson, 1968). Thus, for the ρ-th reactant,

$$-\mathrm{d}n\rho/\mathrm{d}\xi = \xi_{1\rho} \pm \xi_{2\rho}\xi - \xi_{3\rho}\xi^2 \qquad (\rho = 1,\hat{\rho}) \ . \tag{17}$$

The change in the bulk (elemental) composition of $\widetilde{\mathrm{E}}$ with reaction progress (ξ) is given by

$$\mathrm{d}n_\epsilon^{\mathrm{t}}/\mathrm{d}\xi = -\sum_{\rho=1}^{\hat{\rho}} k_{\epsilon\rho}\,(\mathrm{d}n_\rho/\mathrm{d}\xi) \quad . \tag{18}$$

Integration of Eqs. (17) and (18) yields

$$n_\epsilon^{\mathrm{t}}\,(\xi) = n_\epsilon^{\mathrm{t}}\,(\xi = 0) + \sum_{\rho=1}^{\hat{\rho}} k_{\epsilon\rho}(\xi_{1_\rho}\xi + \xi_{2_\rho}\xi^2/2 + \xi_{3_\rho}\xi^3/3) \quad . \tag{19}$$

Temperature may also be varied as a function of reaction progress,

$$T^{c} = T_0^{c} + t_1\xi + t_2\xi^2 + t_3\xi^3 \ . \tag{20}$$

Pressure may be changed in a manner similar to that for temperature, but presently the data base for program EQ6 requires that P be 1 atm (1.013 bar) for $T^c \leq 100°C$ and follow the vapor/liquid equilibrium curve for water for $T^c > 100°C$, or have a constant value of 500 bars for all temperatures. Because reactant dissolution rates and variation in temperature are arbitrary functions specified by the user in defining a problem, functional forms other than the power-series format chosen for Eqs. (17) and (20) could be used. For example, temperature could be defined by a sinusoidal function, if desired. Negative rates of reactant dissolution, however, may be physically unrealistic, so the user should be cautious.

Several types of reaction path models, which have different physical interpretations, can be calculated. Consider the closed system $\widetilde{\mathrm{E}}$, and a system $\widetilde{\mathrm{R}}$ (reactant subsystem) of reactants to be added to $\widetilde{\mathrm{E}}$, along with a reaction vessel $\widetilde{\mathrm{V}}$ (a physical enclosure) in which the reaction takes place. Two kinds of closed system models may be examined: (1) If $\widetilde{\mathrm{V}}$ contains both $\widetilde{\mathrm{E}}$ and $\widetilde{\mathrm{R}}$, then the reaction path is a model of the approach to equilibrium in a closed system ($\widetilde{\mathrm{V}}$) as irreversible reaction occurs between the species in $\widetilde{\mathrm{R}}$ and $\widetilde{\mathrm{E}}$; (2) If $\widetilde{\mathrm{V}}$ contains $\widetilde{\mathrm{E}}$ alone then the path is a model of the final equilibrium states of a sequence of compositionally different systems. If $\widetilde{\mathrm{E}}$ initially consists only of an aqueous solution, then reaction progress (ξ) may be interpreted as the reactant/water ratio.

The only possible mathematical difference between these two models is that one or more of several reactant species might saturate with the aqueous phase and then later be destroyed as other reactants continue to react irreversibly. In the first model, such a reactant should be destroyed reversibly (at equilibrium), whereas in the second its input to $\widetilde{\mathrm{E}}$ remains as arbitrarily specified by Eq. (17). The requirement for the first model can be satisfied by transferring the unreacted mass of a reactant at saturation from $\widetilde{\mathrm{R}}$ to $\widetilde{\mathrm{E}}$, a simple bookkeeping operation.

An open (flow-through) system model in which product solids are removed from $\widetilde{\mathrm{E}}$ to a "physically removed" system $\widetilde{\mathrm{X}}$ permits modelling of compositional changes in a packet of aqueous solution and product mineral zoning, produced as the fluid moves through a reactant medium. Such transfers of mineral masses must take place periodically so that no mineral mass, once precipitated, is later destroyed by back-reaction with the fluid.

USE OF FINITE DIFFERENCES

To obtain good starting estimates at a new point of reaction progress, information at previous points can be used. The technique is based on use of Taylor's series, as was the original method of Helgeson (1968). All estimates of derivatives, however, are based on finite-difference calculations. The high-order predictor-corrector method of Gear (1971a,b) also uses finite-difference expressions to estimate derivatives of order higher than first. His method, however, uses corrector iteration to satisfy a system of ordinary differential (actually, difference) equations, whereas the Newton-Raphson technique used in this work corrects to satisfy the basic algebraic governing equations themselves, and thus avoids propagation of error from one point to another (i.e., "drift").

Suppose that the chemical systems at n successive points of reaction progress ($\xi_n, \ldots, \xi_1$; the subscript 1 denotes the most recent point) have been computed. If there is only one previous point, then a "zero-th" order Taylor's series must be used; i.e., $\underline{z}$ at the previous point must be taken as the vector of starting estimates at the new point. Otherwise, for each k-th element of $\underline{z}$ a vector $\underline{f}$ containing finite differences from order 1 to order n − 1 may be computed (Carnahan *et al.*, 1969, p. 9-10):

$$f_1 = f[12] \equiv f[\xi_1, \xi_2] = (z_{k1} - z_{k2})/(\xi_1 - \xi_2) \tag{21}$$

$$f_j = f[12 \ldots (j+1)] = (f[1 \ldots j] - f[2 \ldots (j+1)])/(\xi_1 - \xi_{j+1}) \quad . \tag{22}$$

The value of each z_k at a new point of reaction progress ξ can be computed as a function of step size $\Delta\xi$ and $\underline{f}$ (Carnahan *et al.*, 1969, p. 11):

$$\begin{aligned} z_k(\xi) = {} & z_k(\xi = \xi_1) + \Delta\xi f_1 + \Delta\xi[\Delta\xi + (\xi_1 - \xi_2)f_2] \\ & + \Delta\xi[\Delta\xi + (\xi_1 - \xi_2)][\Delta\xi + (\xi_1 - \xi_3)f_3] + \ldots \end{aligned} \tag{23}$$

This expression could be used directly to estimate starting values at the new point. However, the finite difference vector $\underline{f}$ may be converted into a vector of derivatives of order 1 through n − 1 by the linear transformation

$$\underline{d} = \underline{\underline{D}}\,\underline{f} \quad . \tag{24}$$

The matrix $\underline{\underline{D}}$ may be calculated by expanding the terms of Eq. (23) and rearranging the resulting terms into the format of a power series in $\Delta\xi$. The Taylor's series expansion corresponding to Eq. (23) is given by

$$z_k(\xi) = z_k(\xi = \xi_1) + (dz_k/d\xi)\Delta\xi + (d^2z_k/d\xi^2)\Delta\xi^2/2! + (d^3z_k/d\xi^3)\Delta\xi^3/3! + \ldots , \tag{25}$$

which also is in the form of a power series in $\Delta\xi$. By equating terms of corresponding order, one may then derive linear relations between the derivatives and finite differences; these may be written in matrix form corresponding to Eq. (24). For up to sixth order,

$$\underline{\underline{D}} = \begin{bmatrix} 1 & a & ab & abc & abcd & abcde \\ 0 & 1 & a+b & ab+ac+bc & \begin{array}{l} abc+dab \\ +dac+dbc \end{array} & \begin{array}{l} abce+dabe+abcd \\ +dace+dbce \end{array} \\ 0 & 0 & 1 & a+b+c & \begin{array}{l} ab+ac+bc \\ +ad+bd+cd \end{array} & \begin{array}{l} abc+dab+dac+dbc \\ +abe+ace+bce+ade \\ +bde+cde \end{array} \\ 0 & 0 & 0 & 1 & a+b+c+d & \begin{array}{l} ab+ac+bc+ad+bd \\ +cd+ae+be+ce+de \end{array} \\ 0 & 0 & 0 & 0 & 1 & a+b+c+d+e \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{26}$$

Here I temporarily abandon earlier convention for symbols and use

$$a = \xi_1 - \xi_2,\ b = \xi_1 - \xi_3,\ c = \xi_1 - \xi_4,\ d = \xi_1 - \xi_5,\ e = \xi_1 - \xi_6, \text{ and } f = \xi_1 - \xi_7 \quad .$$

Starting estimates at new points can then be computed by truncated Taylor's series corresponding to Eq. (25). The accuracy can be controlled by constraining the step size $\Delta\xi$ to keep the contribution from the highest term from exceeding a desired tolerance. The standard assumption, also made by Gear (1971a,b) for integrating ordinary differential equations, is that the ignored terms of higher order are negligible. Experience with program EQ6 has shown that this assumption is sometimes grossly invalid. Thus, Taylor's series predictions with truncation after the sixth order may fail to achieve the desired accuracy even though the step size was specifically constrained to do so. This is not a serious problem in EQ6 because Newton-Raphson iteration then reduces the error to the desired tolerance. (If this iteration fails, then the step size is cut until convergence is achieved; this often occurs during rapid drops in oxygen fugacity, which may change by a factor of $10^{20}-10^{70}$ within very small increments of reaction progress.)

The order of Taylor's series must be reduced to zero whenever a point of reaction progress is reached at which the derivatives are not continuous. Such points arise because of (1) additions to or deletions from the phase assemblage, (2) exhaustion of a reactant, or (3) saturation of a reactant. Because it requires computing time to build up the order and step size after the order has been reduced to zero, the cost of computing a path segment increases rapidly with the number of such discontinuities.

THE FLOW-THROUGH MODEL

Computation of an open system model in which a packet of fluid flows through a reactant medium, which may be a source of elements and/or a source or sink of heat, requires some special treatment. Solid product phases, once formed, are left behind by the flowing packet of fluid and thus may not back-react with it. This can be modelled by periodically transferring product solids from the subsystem $\tilde{E}$ to the physically removed subsystem $\tilde{X}$, a simple bookkeeping operation. The frequency of this operation defines the resolution of the model. For the special case of products of fixed composition, such shifts need not be performed at arbitrary intervals, but only when the mass of such a product achieves a maximum in the equilibrium subsystem. I shall discuss this special case in some detail.

A Taylor's series can be used to estimate the first derivative of the k-th element of $\underline{z}$ (including the logarithmic masses of mineral species):

$$dz_k/d\xi(\xi) = (dz_k/d\xi)(\xi = \xi_1) + (d^2z_k/d\xi^2)\Delta\xi + (d^3z_k/d\xi^3)\Delta\xi^2/2! + \ldots \qquad (27)$$

In principle, this permits calculation of simple maxima of the masses of product minerals. In practice, however, undesirably small step sizes are required to keep the above expression sufficiently accurate to avoid calculating many false maxima. A better approach is to reduce step size to keep only the product-phase masses themselves (and other elements of $\underline{z}$) accurate, and to ignore predicted maxima calculated from Eq. (27) unless the predicted increment of destroyed mass exceeds a trivial value.

Maxima of mineral masses, however, usually do not occur on intervals where the functions (masses) are differentiable. They tend to occur at discontinuities where a new phase appears in the system, the new phase competing with a pre-existing one for the available material. Thus, the location of phase boundaries should be estimated from Taylor's series and the step size appropriately restricted when computing this type of model.

A mineral phase whose mass maximizes should, in theory, disappear entirely from the equilibrium subsystem and hence from the Jacobian matrix. However, because maxima are not precisely located by the practice recommended above, and because mineral masses may be transferred periodically to the physically-removed subsystem for convenience, it is necessary to leave a trivial, sacrificial amount of each mineral in the equilibrium subsystem.

It is necessary here to distinguish between "linear" mass (n) and its derivatives, and logarithmic mass (ℓ) and its derivatives. Let $n^{(k)}$ symbolize the former and $\ell^{(k)}$ the latter; k denotes the order. Then $n^{(0)} \equiv n$ and $\ell^{(0)} \equiv \ell$. At a transfer point, for any mineral, n is replaced by the trivial value n^*. Its derivatives ($n^{(k)}$, $k \geq 1$) are not affected by the transfer. However, the derivatives of logarithmic mass ($\ell^{(k)}$, ≥ 1) must be rescaled to new values ($\ell^{(k)*}$, $k \geq 1$) consistent with the trivial logarithmic mass ℓ^* (=log n^*). It is easiest to do this by first computing the $n^{(k)}$ values from the $\ell^{(k)}$ values which are normally dealt with, transferring all but the trivial mass, and then computing the new $\ell^{(k)*}$ values from the $n^{(k)}$ values and n^*. One may accomplish this by applying the following sequence of equations:

$$n^{(0)} = n \qquad (28)$$

$$n^{(k)} = 2.303 \sum_{i=1}^{k} \binom{k-1}{i-1} n^{(k-i)}\ell^{(i)}, \text{ for } k \geq 1 \qquad (29)$$

$$n^{(0)} = n^* \qquad (30)$$

$$\ell^{(0)*} = \log n^* \qquad (31)$$

$$\ell^{(1)*} = n^{(1)}/(2.303\ n^*) \tag{32}$$

$$\ell^{(k)*} = (1/n^*) \left[(n^{(k)}/2.303) - \sum_{i=1}^{k-1} \binom{k-1}{i-1} n^{(k-i)} \ell^{(i)*} \right], \text{ for } k \geq 2, \tag{33}$$

where $\binom{k-1}{i-1}$ is a binomial coefficient. To derive Eq. (29), use the chain rule of differentiation to evaluate the expression

$$n^{(k)} = (d^k/d\xi^k)\ 10^{\ell}. \tag{34}$$

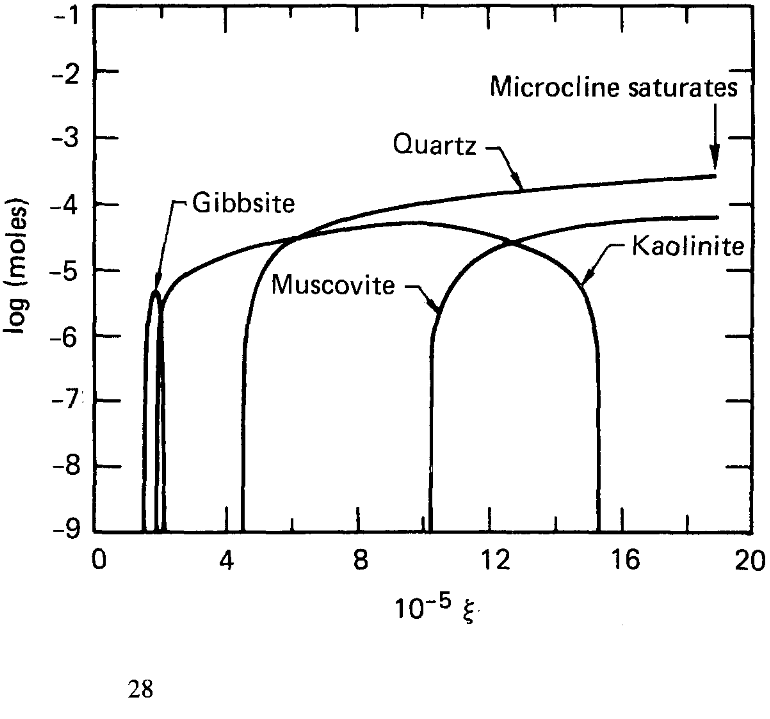
Then invert the results and replace n by n* to obtain Eqs. (32) and (33).

EXAMPLE: DISSOLUTION OF MICROCLINE

Models of the reaction of microcline ($KAlSi_3O_8$) with pH 3 HCl solution at 25°C and 1.013 bars pressure were calculated for both closed and flow-through (open) systems. The mass of the initial aqueous solution was chosen to contain 1000 g H_2O (solvent). The reaction progress variable (ξ) was made directly equivalent to the mass (in moles) of destroyed microcline. One may interpret the closed system results as representing either irreversible reaction of microcline with the HCl solution or titration of the solution by the mineral. This equivalence in physical interpretation is guaranteed by there being but a single reactant (microcline).

Reaction in both closed and open systems produces, in this case, the same suite of product minerals in the same order of appearance: gibbsite, $Al(OH)_3$; kaolinite, $Al_2Si_2O_5(OH)_4$; quartz, SiO_2; and muscovite, $KAl_3Si_3O_{10}(OH)_2$ (Figs. 1 and 2). In the closed system, both gibbsite and kaolinite appear transiently; they are destroyed before the solution saturates with respect to microcline and reaction stops. Gibbsite begins to dissolve when kaolinite appears and competes with it for aluminum. Kaolinite behaves similarly at the appearance of muscovite. In the open system (Fig. 2), the masses of precipitated gibbsite and kaolinite are not subject to dissolution. Active precipitation merely ceases. Physically, this corresponds to the packet of fluid moving through a microcline medium, leaving all precipitate masses behind. Saturation with microcline occurs sooner in the open system because backreaction of transient precipitates does not occur.

Fig. 1. Masses of product minerals (relative to an initial 1000g H_2O) formed by closed system reaction of microcline with pH 3 HCl solution at 25°C and 1.013 bars pressure. Note the transient occurrence of gibbsite and kaolinite.



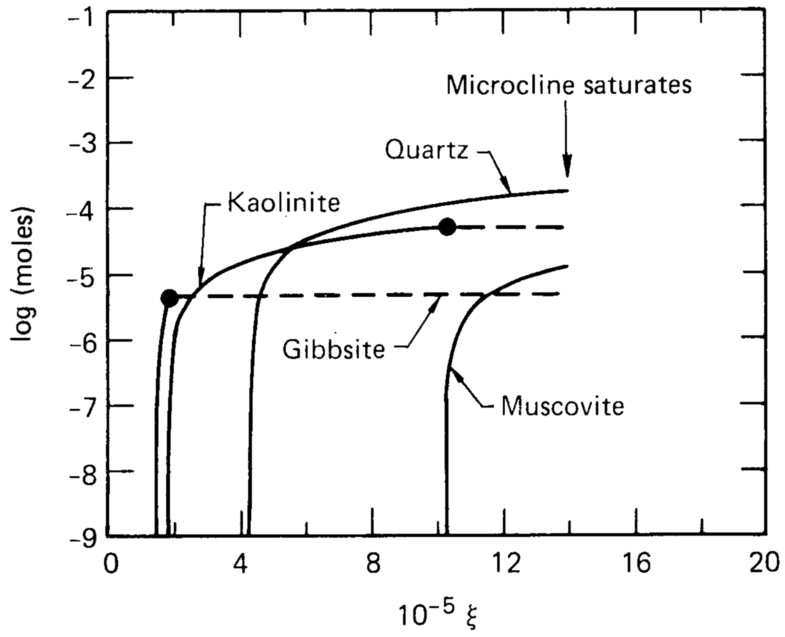


Fig. 2. **Cumulative masses of product minerals (relative to an initial 1000 g H_2O) formed by reaction at 25°C and 1.013 bars of HCl solution of original pH 3 flowing through a microcline medium. Dashed lines indicate lack of further precipitation.**

The reaction paths in both closed and open systems are traced on the K^+/H^+ vs SiO_2° and $Al^{+++}/3H^+$ vs K^+/H^+ activity diagrams in Figs. 3 and 4. Quartz appears at B′ (open system) and D (closed system). The activity of SiO_2° becomes fixed when quartz appears. Therefore, one may interpret the part of Fig. 4 to the right of point D (closed system) or point B′ (open system) as a cross-section of Fig. 3 along the part of the quartz saturation line above D or B′.

On both diagrams the open system path is identical to that of the closed system, except for the dashed line B-B′-D. Gibbsite first appears at A, and kaolinite at B. In the closed system gibbsite is destroyed along the segment B-C, which represents a redirection of the reaction path in activity space. However, the open system path is not redirected because the gibbsite that has precipitated is merely removed from the system. After quartz appears, the activity of dissolved silica is fixed on the quartz line. At E, muscovite appears. The closed system remains fixed at this point until all kaolinite is destroyed. At F the solution saturates with respect to microcline and no further reaction occurs.

The thermodynamic driving force of the irreversible reaction of microcline with this HCl solution is the affinity of the microcline to dissolve. Figure 5 shows this function for both closed and flow-through systems. Note that this is not a linear function of reaction progress; it has a complex dependence on the evolution of the fluid composition.

EXAMPLE: HEATING OF SALTON SEA WATER

EQ3/6 predicted the effects of heating Salton Sea water (Table 9) to 220°C by similar calculations. The temperature in °C was made directly equivalent to ξ, and the calculation began at $\xi = 25$ ($T = 25°C$). The pressure was 1.013 bars below 100°C, and at the steam saturation value at higher temperatures. One may visualize this open system model as a packet of aqueous solution flowing down a pipe with an externally imposed temperature gradient.

The fluid was initially supersaturated with respect to eight phases: magnetite, Fe_3O_4; hematite, Fe_2O_3; calcite, $CaCO_3$; huntite, $CaMg_3(CO_3)_4$; magnesite, $MgCO_3$; aragonite, $CaCO_3$; dolomite, $CaMg(CO_3)_2$; and gypsum, $CaSO_4.2H_2O$. EQ6 calculated the stable assemblage to be aqueous solution-gypsum-dolomite-hematite. The reaction paths then calculated are presented in Figs. 6 and 7 (closed and open systems). In both systems, heating to 220°C produced only two new precipitates, anhydrite and magnesite. In the closed system anhydrite replaced gypsum at about 90°C, and magnesite replaced dolomite near 137°C. In each case both phases co-exist in a small interval of temperature. In the open system, active precipitation of gypsum and hematite ceases as heating begins; the moderate quantity of gypsum removed from the system delays the appearance of anhydrite until about 100°C. However, magnesite appears at essentially the same temperature as in the closed system (137°C).

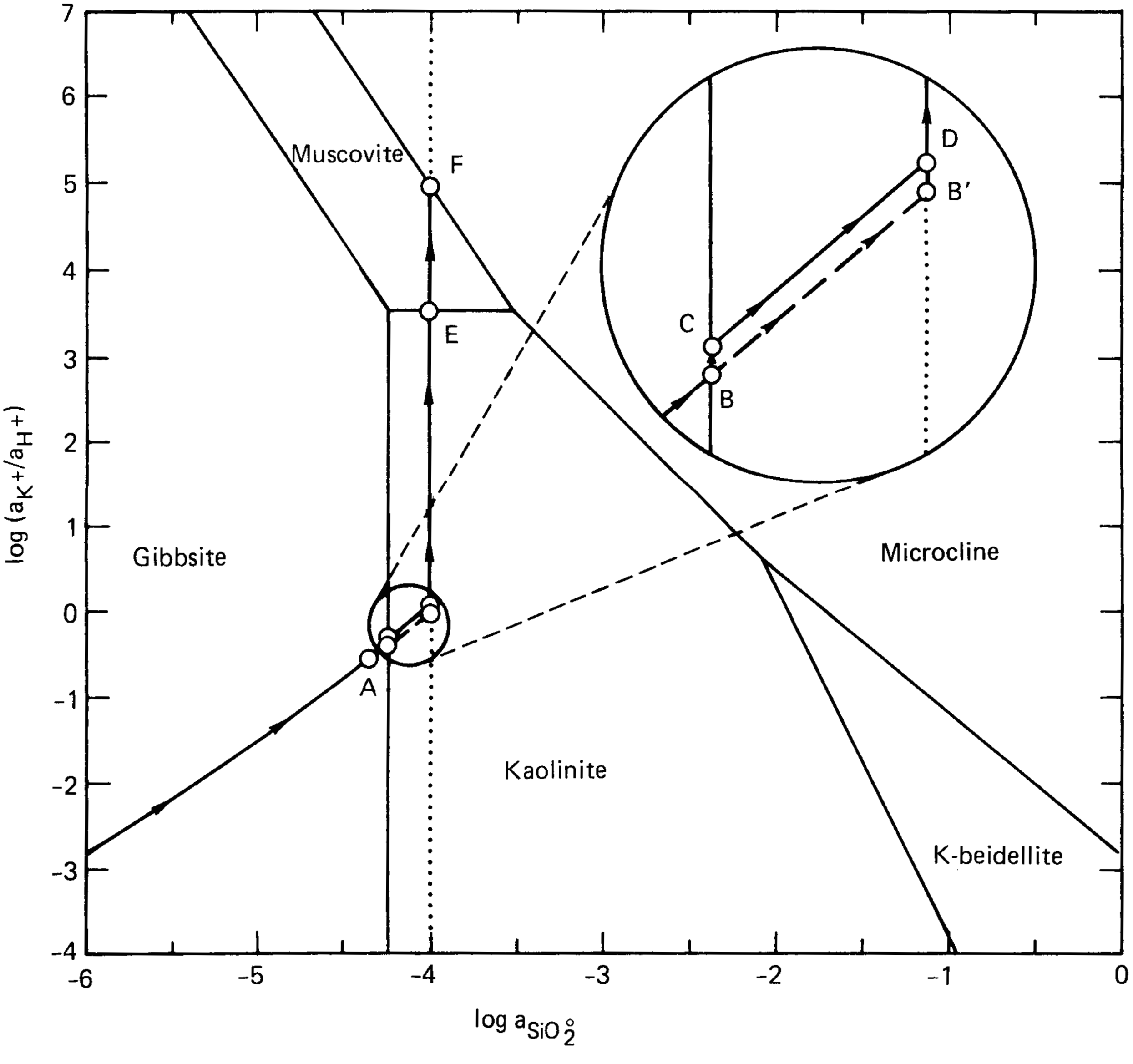


Fig. 3. Reaction of microcline with pH 3 HCl solution at 25°C and 1.013 bars projected on the K^+/H^+ vs SiO_2^o activity diagram. The solid line (with arrows) shows the closed system path. The dashed line, B-B′-D in the magnified inset, shows the flow-through system path where it differs from that of the closed system. A) gibbsite appears; B) kaolinite appears; B′) quartz appears (open system); C) gibbsite disappears (closed system); D) quartz appears (closed system); E) muscovite appears; F) the aqueous solution saturates with respect to the reactant, microcline, and no further reaction occurs.

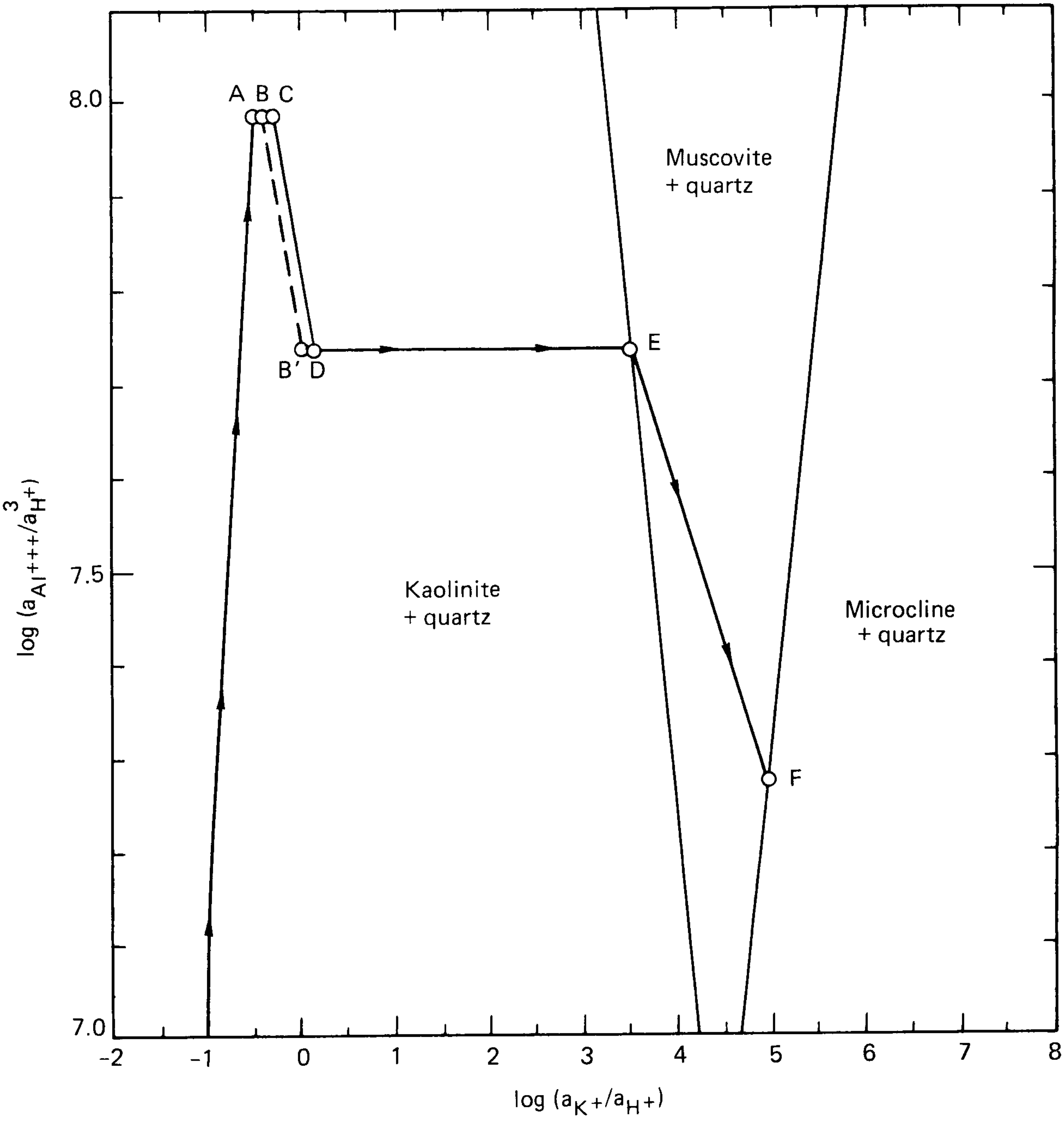


Fig. 4. **Reaction of microcline with pH 3 HCl solution at 25°C and 1.013 bars projected on the $Al^{+++}/3H^+$ vs K^+/H^+ activity diagram. The solid line (with arrows) shows the closed system path, and the dashed line B-B′-D shows where the flow-through system path is different. Lettered points are the same as in Fig. 3.**

Fig. 5. Affinity of microcline to dissolve during reaction with pH 3 HCl solution. The solid line represents the closed system and, up to A, the flow-through system. The dashed line A-F′ represents the rest of the flow-through system curve. Points A through D have the same meanings as in Fig. 3. E) muscovite appears (closed system); E′) precipitation of kaolinite ceases (flow-through system); E″) kaolinite disappears (closed system); F) microcline saturates (closed system); F′) microcline saturates (flow-through system).

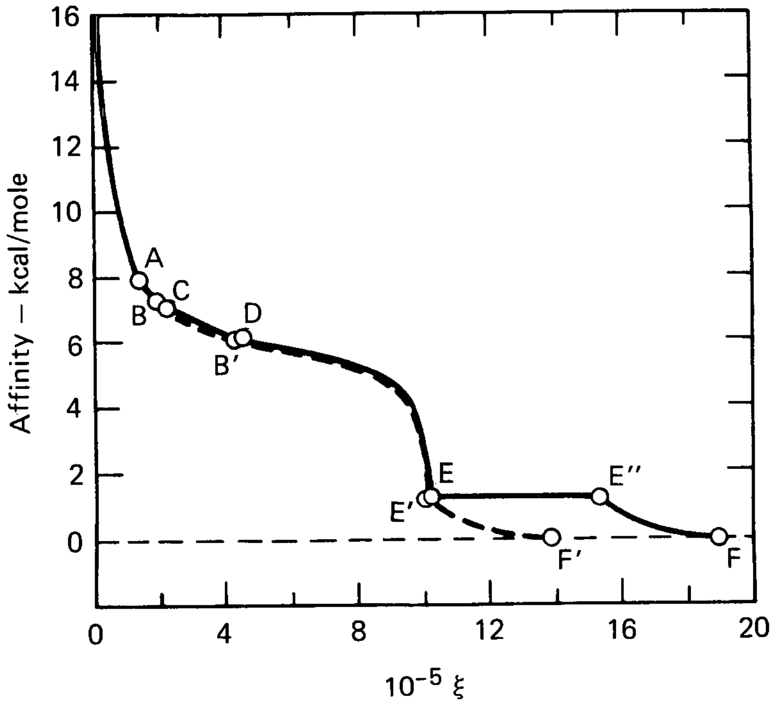


Fig. 6. Masses of precipitates from Salton Sea water (relative to an initial 1000 g H_2O) produced by heating in a closed system. Pressure is 1.013 bars below 100°C and the steam saturation value at higher temperatures. Gypsum, dolomite, and hematite are initial precipitates from supersaturated solution.

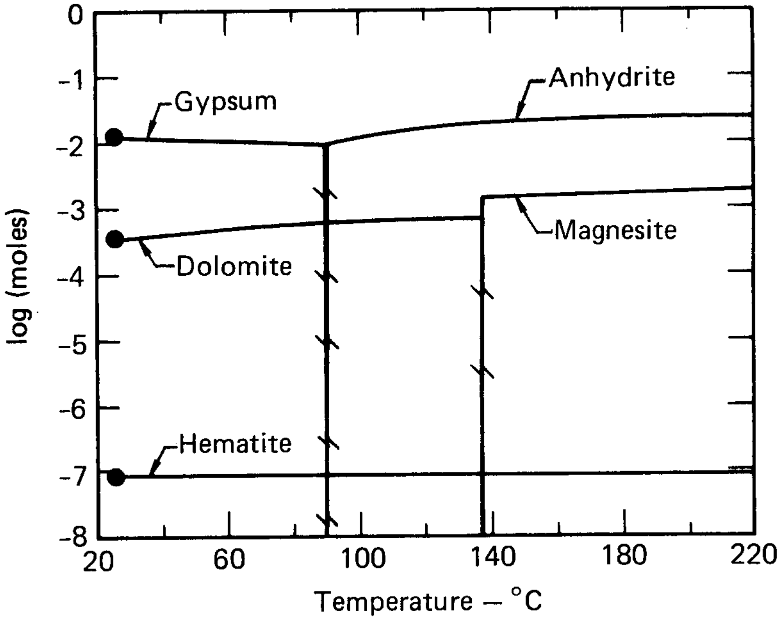


Table 9. Composition of Salton Sea water.[1] Temperature = 25°C, pH = 7.7, oxygen fugacity = 0.21 (atmospheric value).

Component	Molality
Na^+	0.4613
K^+	0.004443
Ca^{++}	0.02404
Mg^{++}	0.04479
Cl^-	0.4274
$SO_4^=$	0.08566
ΣCO_2	0.003366
Fe	1.8×10^{-7}

[1] California Dept. of Water Resources (1970, Table A-5).

Salton Sea water has been proposed for use as cooling fluid for power plant condensers and as make-up fluid for injection into geothermal fields in the Imperial Valley of California. In each case the water will be heated. The results of equilibrium calculations should be applied here with some caution. The precipitation of hematite in this example may be unrealistic. In this relatively short time a hydrated, metastable, probably amorphous iron oxide, $Fe(OH_3)$, would probably form from supersaturated solution instead of the stable hematite. Besides, real Salton Sea water is probably not hematite-supersaturated, because iron in colloidal particles, perhaps $Fe(OH)_3$, probably contributes to the analyzed value for dissolved iron. A more serious problem may be that dolomite does not precipitate at low temperatures except perhaps over geologic time.

The kinetics of precipitation and dissolution of gypsum and anhydrite and, at high temperatures, magnesite, are sufficiently rapid that the models probably give a realistic degree of plugging that would occur during injection of the water into a geothermal field. Figure 8 depicts the calculated volume of total precipitates per 1000 g H_2O that would occur in closed and flow-through systems. About half of the precipitate at 220°C could be eliminated if, before injection, gypsum were allowed to precipitate from supersaturated solution at 25°C and then were removed by settling or filtration.

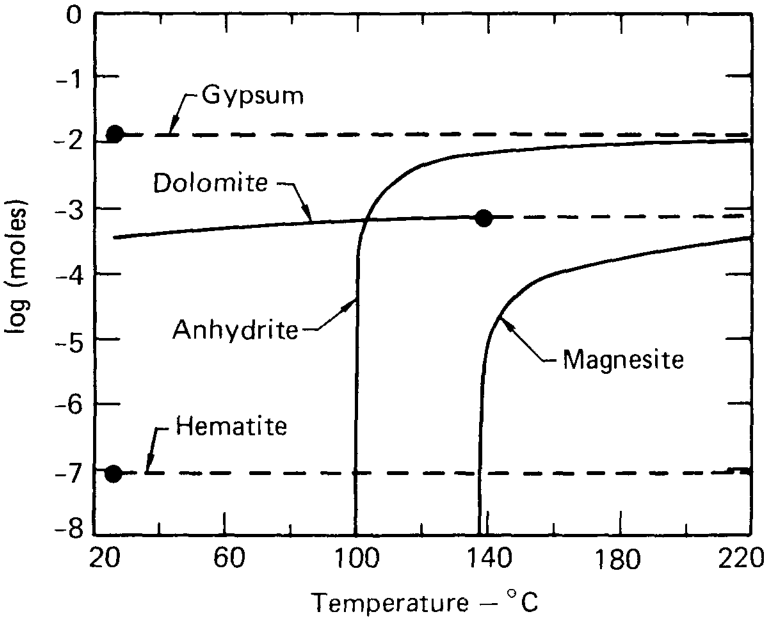
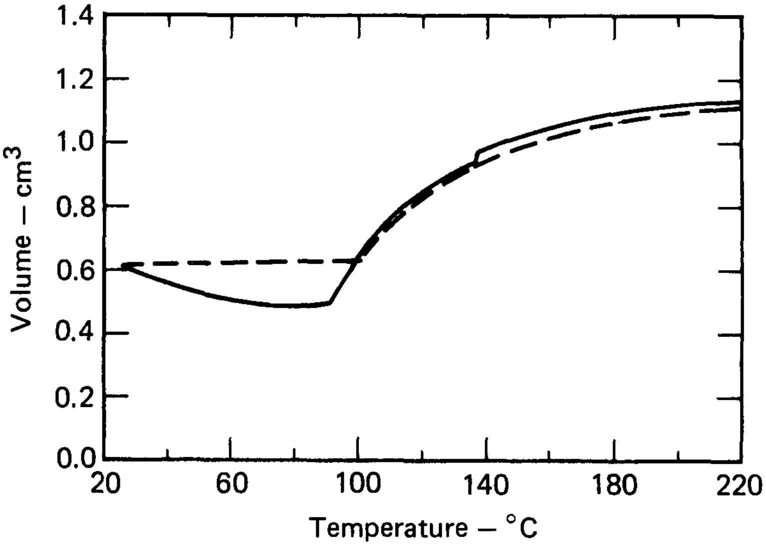


Fig. 7. Cumulative masses of precipitates from Salton Sea water (relative to an initial 1000 g H_2O) produced by heating in a flow-through system. Pressure is 1.013 bars below 100°C and the steam saturation value at higher temperatures. The dashed lines indicate cessation of precipitation. Gypsum, dolomite, and hematite are initial precipitates from supersaturated solution.

Fig. 8. Total precipitate volume per 1000 g H_2O produced by heating Salton Sea water. The solid line represents the closed system and the dashed line the flow-through system.



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APPENDIX A
CONTENTS OF THE EQ3/6 SOFTWARE PACKAGE

The EQ3/6 software package consists of sixteen files written on magnetic tape. These are, in order,

1.	DEQ500B	(a data file)
2.	DEQ500L	(a data file)
3.	DEQ500S	(a data file)
4.	DEQCDL	(a data file)
5.	DEQCDS	(a data file)
6.	DEQCE	(a data file)
7.	DEQREM	(a data file, contains text and documentation)
8.	DEQSSCB	(a data file)
9.	DEQSSCL	(a data file)
10.	DEQSSCS	(a data file)
11.	EQ3	(source code, distribution-of-species program)
12.	EQ6	(source code, "path" program)
13.	EQF	(source code, utility program)
14.	EQS	(source code, utility program)
15.	TEST3	(EQ3 documentation input decks)
16.	TEST6	(EQ6 documentation input decks).

The ten data files contain the following:

Compositions and reactions

1. DEQCE:
   Composition data for elements, aqueous species, minerals, gases, and solid solutions. Also invariant properties of aqueous species such as electrical charge.
2. DEQCDL:
   Coefficients for destruction/dissolution reactions of aqueous species, minerals, and gases, written in terms of an expanded basis set of aqueous species.
3. DEQCDS:
   Coefficients for destruction/dissolution reactions of aqueous species, minerals, and gases, written in terms of a strict basis set of aqueous species. (Created from DEQCDL by utility program EQS.)

Data for the 1 atm-steam saturation curve

4. DEQSSCB:
   Temperature-dependent data, including log K values for the reactions as written in the expanded basis format, at temperatures of 0, 25, 60, 100, 150, 200, 250, and 300°C. Also coefficients for the excess Gibbs energy functions of solid solutions. This file is meant to be read only by the utility program EQF, never by the principal programs EQ3 and EQ6.
5. DEQSSCL:
   Polynomial coefficients for all temperature-dependent data (including log K functions for reactions written in the expanded basis format) plus coefficients for the excess Gibbs energy functions of solid solutions. (Created from DEQSSCB by utility program EQF.)
6. DEQSSCS:
   Polynomial coefficients for all temperature-dependent data (including log K functions for reactions written in the strict basis format) plus coefficients for the excess Gibbs energy functions of solid solutions. (Created from DEQSSCL by utility program EQS.)

Data at a constant pressure of 500 bars

7. DEQ500B:
   Analog of DEQSSCB
8. DEQ500L:
   Analog of DEQSSCL

9. DEQ500S:
Analog of DEQSSCS

Source information

10. DEQREM:
Remarks concerning the structure of the data file package, its application, and the source of the data.

EQ3 and EQ6 do not directly read the DEQ-files, but rather two disk files called DATA1 and DATA2. These files are created at the start of job execution by merging, copying, or renaming the appropriate combination of DEQ-files. Inclusion of the remarks file DEQREM is optional and results only in its being printed on the job's output.

EQ3:

DATA1 = DEQCE
DATA2 = DEQCDL,DEQSSCL(,DEQREM) for ssc pressures
= DEQCDL,DEQ500L(,DEQREM) for 500 bars pressure

EQ6:

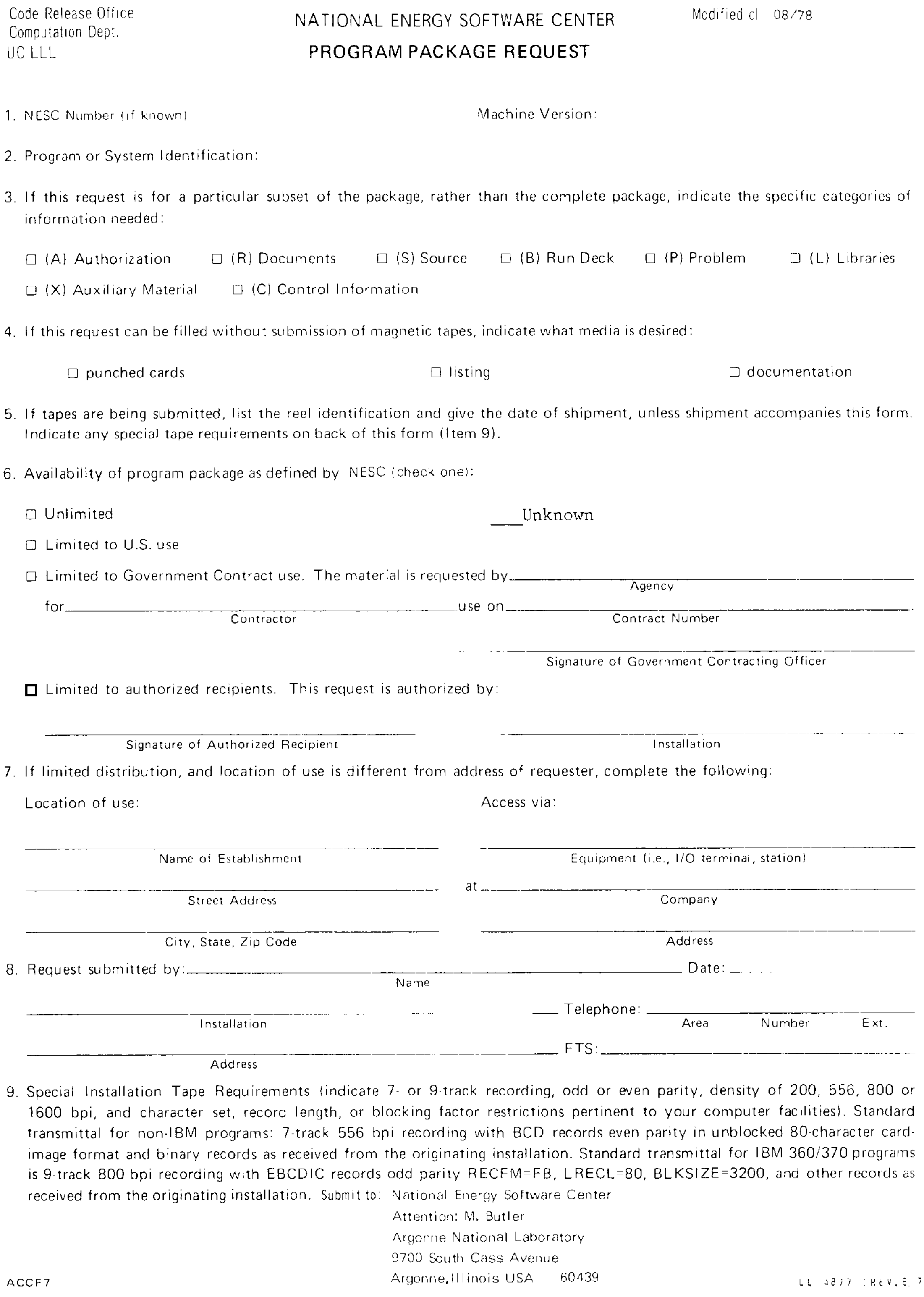
DATA1 = DEQCE and DEQCDS
DATA2 = DEQSSCS (and DEQREM) for ssc pressures
= DEQ500S (and DEQREM) for 500 bars pressure

On the CDC 7600 computer, EQ3 requires about 100K (octal) words of memory and typically uses a few CP seconds to process each input deck. EQ6, on the other hand, requires 147K SCM and 3K LCM memory. Execution times depend strongly on the nature of the input and may range from a few CP seconds for a short problem to a few minutes for a very long one.

Utility routine EQF fits interpolating polynomials to the gridded data in DEQSSCB (DEQ500B) to produce the file DEQSSCL (DEQ500L). EQS checks the consistency among the compositional, electrical charge, and reaction coefficient data and creates the files DEQCDS and DEQSSCS (DEQ500S).

APPENDIX B

SAMPLE REQUEST FORM TO OBTAIN THE PACKAGE FROM THE NATIONAL ENERGY SOFTWARE CENTER



Code Release Office
Computation Dept.
UC LLL

NATIONAL ENERGY SOFTWARE CENTER
PROGRAM PACKAGE REQUEST

Modified cl 08/78

1. NESC Number (if known) Machine Version:

2. Program or System Identification:

3. If this request is for a particular subset of the package, rather than the complete package, indicate the specific categories of information needed:

☐ (A) Authorization ☐ (R) Documents ☐ (S) Source ☐ (B) Run Deck ☐ (P) Problem ☐ (L) Libraries
☐ (X) Auxiliary Material ☐ (C) Control Information

4. If this request can be filled without submission of magnetic tapes, indicate what media is desired:

☐ punched cards ☐ listing ☐ documentation

5. If tapes are being submitted, list the reel identification and give the date of shipment, unless shipment accompanies this form. Indicate any special tape requirements on back of this form (Item 9).

6. Availability of program package as defined by NESC (check one):

☐ Unlimited ___Unknown

☐ Limited to U.S. use

☐ Limited to Government Contract use. The material is requested by________ Agency

for________ Contractor use on________ Contract Number.

________ Signature of Government Contracting Officer

☐ Limited to authorized recipients. This request is authorized by:

________ Signature of Authorized Recipient ________ Installation

7. If limited distribution, and location of use is different from address of requester, complete the following:

Location of use: Access via:

________ Name of Establishment ________ Equipment (i.e., I/O terminal, station)

________ Street Address at ________ Company

________ City, State, Zip Code ________ Address

8. Request submitted by:________ Name Date:________

________ Installation Telephone:________ Area Number Ext.

________ Address FTS:________

9. Special Installation Tape Requirements (indicate 7- or 9-track recording, odd or even parity, density of 200, 556, 800 or 1600 bpi, and character set, record length, or blocking factor restrictions pertinent to your computer facilities). Standard transmittal for non-IBM programs: 7-track 556 bpi recording with BCD records even parity in unblocked 80-character card-image format and binary records as received from the originating installation. Standard transmittal for IBM 360/370 programs is 9-track 800 bpi recording with EBCDIC records odd parity RECFM=FB, LRECL=80, BLKSIZE=3200, and other records as received from the originating installation. Submit to: National Energy Software Center
Attention: M. Butler
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois USA 60439

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APPENDIX C
NOTE ON THERMODYNAMIC DATA

Two parallel sets of thermodynamic data were constructed to support theoretical prediction of rock-water interactions. The first corresponds to a pressure of 1 atm (1.013 bar) for the temperature range 0-100°C and to steam saturation pressure above that. The second set corresponds to a constant pressure of 500 bars. Temperature-dependent data were computed or compiled in each case at temperatures of 0, 25, 60, 100, 150, 200, 250, and 300°C and fitted to interpolating polynomials to support calculations at any value in the range 0-350°C.

The thermodynamic data were taken mainly from Helgeson and Kirkham (1974ab, 1976) and Helgeson *et al.* (1978). These sources form an internally consistent and fairly comprehensive set of data for water, dissociated ions, and rock-forming minerals. Because complete data for certain clay minerals (especially smectites) and chlorites relevant to many aqueous geochemical systems are not given, it was necessary to estimate some or all of their thermodynamic functions (free energies of formation, enthalpies, entropies, volumes, and heat capacity coefficients) using techniques suggested by Tardy and Garrels (1974) and Helgeson *et al.* (1978). The details of these calculations and the resulting estimates are given by Wolery (1978, Appendix B). Values of log K for mineral dissolution reactions and redox (cross-link) reactions among aqueous species were then calculated from the above data using the computer program SUPCRT (Helgeson *et al.*, 1978) for the eight discrete temperatures and appropriate values of pressure.

Values of log K for the dissociation of aqueous complexes at pressures for H_2O liquid/vapor equilibrium were taken mainly from Helgeson (1969). However, a number of values were selected from more recent literature. I wish to emphasize that my effort to update these log K values in no way represents a critical and comprehensive compilation, and to point out that uncertainties in complex dissociation data are in general much greater than for mineral dissolution data. Values of log K for complex dissociation reactions at 500 bars pressure were generated from corresponding steam saturation curve values using the dielectric constant correction suggested by Helgeson (1969).

The lack of a satisfactory treatment for most of the solid solutions present in aqueous geochemical systems (especially sheet silicates) usually requires that end-member components or other specific compositions be treated as individual phases. Alternatively, one might model such phases as ideal solutions, but many are obviously quite non-ideal.

Non-ideality in the aqueous phase was treated according to equations and data presented by Helgeson (1969). However, the activity coefficients of neutral, polar complexes such as $CaSO_4^\circ$ were assigned a value of unity rather than that of aqueous CO_2. The activity coefficient of aqueous carbon dioxide increases with increasing ionic strength (Helgeson, 1969), but Reardon and Langmuir (1976) have shown that the activity coefficients of $CaSO_4^\circ$ and $MgSO_4^\circ$ actually decrease at 25°C and 1 atm pressure. We lack sufficient understanding of these parameters at high temperatures and pressures, but the present assumption of unit activity coefficients for such species appears reasonable.