The EQ3/6 Software Package for Geochemical Modeling: Current Status

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EQ3/6 is a software package for modeling chemical and mineralogic interactions in aqueous geochemical systems. The major components of the package are EQ3NR (a speciation-solubility code), EQ6 (a reaction path code), EQLIB (a supporting library), and a supporting thermodynamic data base. EQ3NR calculates aqueous speciation and saturation indices from analytical data. It can also be used to calculate compositions of buffer solutions for use in laboratory experiments. EQ6 computes reaction path models of both equilibrium step processes and kinetic reaction processes. These models can be computed for closed systems and relatively simple open systems. EQ3/6 is useful in making purely theoretical calculations, in designing, interpreting, and extrapolating laboratory experiments, and in testing and developing submodels and supporting data used in these codes. The thermodynamic data base supports calculations over the range 0-300°C.

EQ3/6 (1-3) is a software package consisting of modeling codes, supporting thermodynamic data files, and some data base management software. Its purpose is to calculate models of chemical interactions in aqueous geochemical systems. It was originally written in the period 1975-1978 by T.J. Wolery (1) to compute reaction path models of seawater/basalt interactions under hydrothermal conditions, and was patterned in function after the PATHI code developed by Helgeson et al. (4, 5). It has subsequently been used in a number of other studies (e.g., refs. 6-19) of rock/water or other solid/water interactions at both low and high temperatures. EQ3/6 is presently being developed and applied as part of the U.S. program for disposal of high level nuclear waste (20; 13-19). Various versions of EQ3/6 have been distributed to the scientific community in the past and work is continuing to improve and extend this software package. EQ3/6 was covered by the modeling software survey of Nordstrom et al. (21) in the 1979 Symposium Series predecessor to this volume. A more recent and more detailed review of EQ3/6 has since appeared (22). The most recent release of EQ3/6 is the "3245" version, general distribution of which began in February, 1988. The "3270" version is presently being developed. These versions will be discussed in the present communication.

The EQ3/6 software package consists of several principal components. These are the EQ3NR and EQ6 codes, the EQLIB library, and the thermodynamic data base. The EQLIB library and the thermodynamic data base support both of the main modeling codes. EQLIB contains math routines, routines that perform various computer system functions, and routines that evaluate scientific submodels, such as for activity coefficients of aqueous species, that are common to both EQ3NR and EQ6. The data base covers a wide range of chemical elements and nominally allows calculations in the temperature range 0-300°C at a constant pressure of 1.013 bar from 0-100°C and the steam-liquid water equilibrium pressure from 100-300°C.

EQ3NR (2) is a *speciation-solubility code. It computes a static thermodynamic model of an* aqueous solution, given inputs such as pH and analytical (total) concentrations. The typical output includes the distribution of aqueous species, given both as molal concentrations and thermodynamic activities of individual species and as percentage contributions to total mass balances. It also includes saturation indices, defined as SI = log Q/K, where Q is the ion activity product and K the equilibrium constant of a reaction, typically for the congruent dissolution of a mineral phase. EQ3NR is very flexible, and some important parameters that are normally outputs can be made inputs, and vice versa. For example, one might analyze a solution and input the data to compute the saturation index for a given mineral. But one might also want to ask the question, if the same mineral is assumed to be in equilibrium with the solution, what should be the value of one of the analytical data, given that values for the others are known and correct. EQ3NR can make such calculations.

EQ6 (1, 2; Wolery, T.J., and Daveler, S.A., EQ6 User's Guide, in prep.) is a reaction-path program which operates in a few distinct modes. Typically, it is used to compute the consequences of reacting an aqueous solution, previously defined by running EQ3NR, with a set of specified "reactants." The objective is to model the changing chemistry of the solution and the appearance and disappearance of any product phases. This can be done in a titration mode, a closed system mode, or a pseudo-one-dimensional "flow-through" mode which follows the evolution of a packet of solution moving through a reactant medium. There is no provision in this code for modeling actual flow through a column; the "flow through" mode presently in the code only models what happens to the "first" packet of water. All of the above models can be modified to impose fixed values of fugacity for specified gases (23), corresponding to systems that are open with respect to these species and connected to external reservoirs. This capability is useful in modeling systems which are open to the atmosphere, which contains such highly reactive gases as molecular oxygen and carbon dioxide.

The functions which describe the rates at which the "reactants" react with the aqueous solution are chosen by the user and may represent arbitrary relative rates or actual kinetic rate models. If arbitrary relative rates are employed, no time frame is involved in the calculation and progress is measurable only in the change in the remaining amounts of reactants. This is an "equilibrium step calculation," representing a sequence of equilibrium states corresponding to a system whose gross composition is being changed according to some formula. If the rate functions involved are actual rate laws, such as the one proposed for quartz dissolution and growth by Rimstidt and Barnes (24), then the calculation includes a time frame. The word "reactant" as used here refers to a substance which is not in equilibrium with the system composed of the aqueous solution and any "products" which are in equilibrium with that solution. The rate at which a "reactant" dissolves in the aqueous solution can be negative, in which case the "reactant" is really a product whose formation is governed by a kinetic rate law instead of an instantaneous response to satisfy solubility equilibrium. This is the principle behind an option to compute simulations including precipitation kinetics (25).

The temperature along a reaction path may be constant or variable. In non-kinetic mode, it may be treated as a function of the reaction progress variable. In kinetic mode, it may be treated as a function of time. Therefore, EQ6 can also be used to compute the consequences, such as pH shift and mineral precipitation, of heating or cooling an aqueous fluid (1, 26).

Modeling Pitfalls

Software such as EQ3/6 may be a useful tool in geochemical modeling, but there are a number of potential pitfalls of which the user should be keenly aware before trusting the computed results. EQ3/6 is not a "computerized chemical model" or "black box" whose output is always correct (even approximately) or necessarily meaningful, even if correct. It is really a geochemical "calculator" which allows one to compute models which combine or integrate various submodels. One submodel might describe the aqueous species which are thought to be present in a given system, and any equilibrium relations that should pertain among them. Another might describe the thermodynamic activity of water and the activity coefficients of the aqueous species. A third might be a kinetic rate law for a dissolving mineral. Certain other specifications about the nature of the reacting system also pertain in the combination of these submodels, such as whether the system is closed or open with respect to certain gas species, and whether or not the temperature is constant.

Generally speaking, the submodels are tied in some fashion to experimental data. The user of modeling software such as EQ3/6 needs to be aware of the nature and limitations of such submodels and how well they are connected to actual observations. Submodels are best constrained by studies of simple, carefully defined systems. Unfortunately, it is often difficult or impossible to define experimental systems that completely isolate the effects that one wishes to study. For example, in studies of the dissolution rates of minerals, one would like to obtain results which would pertain to the dissolution behavior of minerals in natural systems. However, artifact effects related to sample preparation may be present in the absence of special precautions (27). Thus, many of the data reported in the older literature are unsuitable for building appropriate rate models, and new studies in which such effects are eliminated or ameliorated (e.g., 27-29) are required.

Because of the difficulty in isolating specific effects, a submodel may be constructed by assuming the validity of a second submodel. For example, solubility product constants may be determined from solubility measurements by assuming a specific model for the activity coefficients of the species in the fluid phase. An inconsistency may result if these constants are later employed in conjunction with a different model of the activity coefficients. The nature of speciation and activity coefficient submodels is such that they should really be considered one model and be developed concurrently. An outstanding example of this approach is the "sea salt" system model of Harvie, Moller, and Weare (30). Inconsistencies may also result by building a submodel, as for speciation, by combining various reported results. This problem is commonly encountered in building large thermodynamic data bases.

It is important to recognize that the use of geochemical modeling software such as EQ3/6 will almost always involve extrapolating submodels beyond the bounds of the experimental data on which they were constructed. For example, in putting together the basis for a calculation simulating the reaction of silicate minerals with ground water, one might choose to utilize the model for quartz dissolution and growth proposed by Rimstidt and Barnes (24). Their model was proposed on the basis of experiments in which the aqueous solution was always neutral to slightly acidic. It reflected no dependence of rate on solution pH. Later experiments by Knauss and Wolery (29) showed such a dependence in the mildly alkaline to alkaline pH range. Further experiments might show other dependencies that could be significant under conditions of interest to users of modeling codes.

A given set of experimental data may be explainable by different models. For example, Reddy et al. (31) measured the growth rate of calcite and fit the data to a rate law model proposed by Plummer et al. (32). It was later shown (22) that a very simple "transition state theory" rate law, quite different in form, fit the data about as well (neither model fit the data perfectly). One should keep in mind that such models may extrapolate differently.

Models are often developed to explain certain kinds of data, ignoring other kinds that also might be pertinent. The initial development of Pitzer's equations (33, 34) for activity coefficients in concentrated solutions was focused on explaining measurements of vapor pressure equilibrium and of electromotive force (emf). The data could be explained by assuming that the electrolytes examined were, at least in a formal sense, fully dissociated. Later work using these equations to explain solubility data required the formal adoption of a few ion pair species (30). Even so, no speciation/activity coefficient model based on Pitzer's equations is presently consistent with the picture of much more extensive ion-pairing based on other sources, such as Smith and Martell's (35) compilation of association constants. This compilation is a collective attempt to explain other kinds of data, such as electrical conductance, spectrophotometry, and acoustic absorption.

Other problems may arise if the modeler's objective is to explain or predict the results of an "applications level" experiment (one involving a relatively complex system) that is carried out in the field or, more commonly, the laboratory. First, the conditions assumed to prevail in the experiment may not be the actual ones. For example, the experiment may be thought to be a closed system, when in fact there is loss or gain of volatiles such as carbon dioxide. For another, the walls of the experimental vessel may be thought to be not a factor in the course of reaction when in fact they are via such mechanisms as diffusive absorption or corrosion.

A more difficult problem is that the user of a modeling code such as EQ6 must specify whether a given reaction is controlled by partial equilibrium, is governed by a rate law, or simply does not proceed on the time scale of interest. This issue can not be conveniently addressed by reference to some data base, but requires user cognizance of what sort of behavior has been observed in similar systems. Often, a number of such experiments must be done and analyzed to build up the necessary experience or "lore" to make successful predictions in an a priori sense. Field observations are an equally important part of such experience if modeling results are to be applied to field scenarios.

A point that often receives insufficient appreciation is that a system in the laboratory often behaves differently in sometimes critical ways from what is nominally the same system in the field. If one is studying rocks that are the products of natural hydrothermal alteration, the partial equilibrium assumption is more likely to be valid than it is in a laboratory hydrothermal apparatus in which one attempts to recreate such alteration. Such differences are commonly manifested in the appearance of different mineral assemblages, though changes in fluid chemistry may be very similar. An example is hydrothermal reaction of seawater and basalt, a process which occurs naturally at mid-ocean ridges (see refs. 1, 36, and many sources cited therein). The naturally altered basalts become rich in chlorite or chlorite plus epidote. In experimental systems, smectite clays appear instead. Time appears to be the limiting factor.

A further problem facing the user of geochemical modeling software is that no code, even EQ3/6, currently includes provision for all of the possible phenomena that may occur in reacting systems of interest. Beyond that, the fundamental scientific data base to support adequate modeling of all of these phenomena under all possible conditions of interest is incomplete. New fundamental measurements may be necessary to model many systems and scenarios of interest.

The preceding discussion is not intended to leave the reader with the feeling that little can be done with geochemical modeling codes. Much can now be done with them. In general, though, the user must be knowledgeable about the submodels included in the code, the related science base, the options offered by the code, and most importantly, the lore or base of experience concerning the problem. The computer code can then be useful in refining knowledge and testing hypotheses.

The EQ3/6 Software Package

The original version of EQ3/6 was written in FORTRAN 66 on CDC 6400 and 6600 computers at Northwestern University (1). In 1978, Wolery brought EQ3/6 to Lawrence Livermore National Laboratory (LLNL), where it was adapted and further developed on CDC 7600 machines. Some of this work shifted for a time onto Cray computers. A few years ago, almost all development work shifted to 32-bit machines with UNIX-based operating systems. A concurrent shift was made in the programming language, from FORTRAN 66 to FORTRAN 77. A deliberate effort has been made to maintain a high degree of portability of EQ3/6 on all 32- and 64-bit machines which offer full ANSI FORTRAN 77. This includes essentially all 32- and 64- bit UNIX-based machines, VAX machines, and Cray machines. The recent product is not very portable to CDC machines or IBM mainframes. To obtain reasonable run times on smaller problems, EQ3/6 requires a machine at least as powerful as a Sun 3/50 or a VAX 11/780. For larger EQ6 problems, a much faster machine, such as a Cray, Convex, Alliant, or high-end DEC machine is more suitable.

The guiding principle of EQ3/6 development has been to offer the user a a number of modeling options. For each major type of submodel, the approach has been to offer a menu of possibilities. For example, the user chooses the available model for activity coefficients of aqueous species that best fits his current problem. This reflects the belief of the code developers that there is usually no single "best" model to use as the submodel of a given type; rather, there are various models with different strengths and weaknesses. This approach to code development also lets the user investigate the consequences of using alternative models for a given phenomenon.

Generally speaking, the strong points of EQ3/6 include flexibility in terms of allowed input in speciation-solubility calculations, automatic decision-making in reaction path calculations (constrainable a priori by the user by means of the input file), a large thermodynamic data base, capability to treat dissolution and precipitation growth kinetics, a variety of models for treating the activity coefficients of aqueous species, and a significant and growing capability to treat the thermodynamics of solid solution. The principal weak points presently are that no capability is included for explicit treatment of reactions on mineral surfaces (sorption), for even one-dimensional fully coupled transport and chemistry, and pressure corrections for dealing with pressures off the 1.013 bar-steam saturation curve. Sorption modeling is a strong point of other codes, prominent examples being MINEQL (37) and its derivative MINTEQ (38). Plans exist (20) to extend EQ3/6 capabilities to cover such phenomena, where the current scientific base exists.

There is a published user's guide (3) for the EQ3NR code, written to correspond to the 3230 version. The only really significant difference between that and the presently available 3245 version is that the newer code allows the use of Pitzer's equations to describe the activity coefficients of aqueous species (39). The main user's guide for the EQ6 code (written to correspond to the 3245 version) is now in the final stages of preparation. Until it becomes available, the reader is best referred to ref. 2. Several supplementary user's guides have been already published. Ref. 23 describes the option for modeling reaction paths by imposing fixed fugacities of selected gases. Ref. 25 addresses the options for dealing with kinetic rate laws.

Activity Coefficients of Aqueous Species. The original version of EQ3/6 followed Helgeson et al. (5) in using the "B-dot" equation to describe the activity coefficients of aqueous solutes and a recommended approximation for the activity of water. The "B-dot" equation represents a simple extension of the Debye-Hückel equation and is only useful in relatively dilute solutions (deviations from precise measurements can be seen at ionic strengths below 0.1 molal, and become severe above 1.0 m). Beginning with version 3245, EQ3/6 offers two alternatives, the Davies (40) equation and Pitzer's equations (33, 34, 30, 39).

The Davies equation is another simple extended Debye-Hückel model and is generally about as good or bad as the "B-dot" model. The attractive aspect of the "B-dot" and Davies equations is that they are universally applicable to any aqueous species, real or imagined. However, they can not be applied to concentrated solutions. Pitzer's equations can be applied in dilute or concentrated solutions, but require special parameters (virial coefficients) for the species present. There is presently no reliable way to estimate the parameters; instead, they must be fit to experimentally determined quantities, such as the osmotic coefficient. Furthermore, the speciation model one employs using this option must be consistent with that employed in the fitting process. At present, the usage of Pitzer's equations is largely restricted to systems containing strong electrolytes, such as the "sea salt" system studied by Harvie, Moller, and Weare (30).

Three other options are presently being studied, with an eye on including them in the forthcoming 3270 version. One of these is the equations of Helgeson, Kirkham, and Flowers (41), for which further model development is required. The second (42) is based on the hydration theory concept of Stokes and Robinson (43). This also requires further model development. The third set is a model (44) recommended by the European Nuclear Energy Agency for obtaining equilibrium constants for the formation of aqueous complexes of interest in nuclear waste disposal, such as of uranium and plutonium.

In older versions of EQ3/6, no special effort was made to ensure consistency between the activity coefficient equations, which give results for single ions, and any special pH scale. The pH scale governing standard measurements is the NBS scale (45), which is defined in terms of a simple Debye-Hückel model for the activity coefficient of the chloride ion. If one uses the "B-dot" equation for the ions, and makes no corrections, one is essentially defining pH on the "B-dot" scale. Numerically, the inconsistency is small in dilute solutions, and has traditionally been ignored in perhaps all geochemical modeling codes. Beginning with the 3245 version, EQ3/6 now corrects all activity coefficients of aqueous ions to either an extended NBS scale or a "rational" scale, depending on instructions from the user. The NBS scale in the code is said to be extended because the formal limit of 0.1 m ionic strength is ignored. There is an ambiguity in the NBS scale because the correction depends on the ionic strength, which is a model dependent parameter whose value depends on what species one takes to be present. The "rational" scale defines the activity coefficient of the hydrogen ion as unity. The correction for this scale is independent of any model dependent parameters.

Thermodynamic Data Base. The thermodynamic data base was originally a reformatted version of the data base for the PATHI program of Helgeson and coworkers (4, 5; these references say little about this data base). The aqueous speciation model included many ion pairs and aqueous complexes. The PATHI data base had just been updated to conform with the contemporaneous efforts of Helgeson et al. (46-48) to provide better thermodynamic data. This affected the equilibrium constants for mineral dissociation reactions and a few aqueous redox reactions, but left the data for ion-pairing and complexation reactions unchanged. The mineral data on the first EQ3/6 data base were supplemented by Wolery (1) with some estimates of the constants for a number of clay mineral compositions.

Since EQ3/6 was brought to LLNL, the data base has been periodically updated and expanded. A particular effort has been made to respond to the subsequent efforts of Helgeson's group, which has done much work to correlate and predict the thermodynamic properties of the major rock-forming minerals (mostly exclusive of evaporite minerals) and many of the major aqueous solutes found in natural geochemical systems. The data for evaporite minerals were taken from the work of Harvie, Moller, and Weare (30). Other data base development has taken place in response to needs in the areas of radionuclide migration and disposal of high level nuclear waste. These efforts include Rard's work on the thermodynamics of species of technetium (49) and ruthenium (50). A complete documentation of all these changes is beyond the scope of the present communication.

The most recently released version of the EQ3/6 data base (3245; Feb. 1988) contains data for 47 chemical elements, 686 aqueous species, 638 aqueous reactions, 713 pure minerals, 11 gases, and 15 solid solutions. The data base itself is generally known by the file name of DATA0. The modeling codes do not read DATA0, but an unformatted equivalent known as DATA1. In the process of writing DATA1, a preprocessor performs various checks (such as to ensure that all reactions satisfy mass and charge balance) and replaces equilibrium constants on a temperature grid with equivalent interpolating polynomials. The preprocessor makes a special DATA1 to support the use of Pitzer's equations. An additional data file containing the Pitzer interaction parameters is read and all aqueous species that appear on DATA0 but not this file are stripped out to maintain consistency between the activity coefficient and speciation models. The interaction parameters on the additional data file are all of the thermodynamically observable type; these are broken down following a set of arbitrary conventions to non-observable theoretical equivalents to facilitate calculation of single-ion activity coefficients.

The DATA0 file was formerly maintained by a combination of hands-on editing, the use of a data block editing code, and the use of several data-generating codes, each of which had one or more of its own data files. This patchwork system has been replaced by a system based on INGRES, a commercial relational data base. There is a unified master data file, which, unlike DATA0, contains thermodynamic data in different forms (e.g., Gibbs energies, enthalpies, entropies, and heat capacities). The previously used data base codes have been integrated into the system as INGRES "applications." Internal documentation of the data and how it has been processed is an integral part of the system. The application code for adding to and updating the master data file generates audit records of all changes. Additional modifications in progress include provisions for the correction of apparent equilibrium constants to standard state values, for consistent treatment of multiple activity coefficient formalisms, and for ensuring compatibility with values recommended by CODATA and the NEA. The problem of multiple activity coefficient/speciation formalisms will be treated in future releases by generation of separate DATA0 files. Also in preparation is a major update in response to recent work by Helgeson and colleagues (51, 52; Schock, E.L., and Helgeson, H.C., Geochim. Cosmochim. Acta, submitted; Schock, E.L., Helgeson, H.C., and Sverjensky, D.A., Geochim. Cosmochim. Acta, submitted). Beginning in late 1988, LLNL will start issuing, on a regular basis, updated versions of DATA0 files.

Solid Solutions. EQ3/6 includes provision for dealing with solid solutions, both as "reactant" and "product" phases. Both ideal and non-ideal solid solution models have been incorporated. The compositions of "product" solid solutions continually readjust to remain in equilibrium with the changing fluid composition. In the "flow-through" open system mode, "product" solid solutions are removed from the reacting system as they form, resulting in zoning along the flow path. In the other modes, the entire mass of such phases reequilibrates with the fluid. The treatment of solid solution "reactants" is straightforward; the user defines the specific compositions on the input file. The treatment of "product" solid solutions is complicated by the fact that the saturation index for a solid solution is a function of its composition. Until the solid solution actually forms, however, the value of the saturation index is indeterminate. The approach taken in EQ3/6 is to use the maximum value over the composition space of the phase.

Application of EQ3/6 to many important problems will depend critically on the ability to model compositional variation in clays and zeolites. Thermodynamic data for 2:1 clays, and to a lesser extent zeolites, are not sufficiently abundant or of high enough quality to construct definitive solid solution models for these phases. Nevertheless, incorporation of reasonable models into EQ3/6 is a prerequisite to assessing the sensitivity of the geochemical modeling results to different solid solution approaches and for testing predictions against experimental and field observations.

In the 3245 version of EQ3/6, the solid solution models are restricted to the molecular-mixing type. Included for example is a 12 component model for dioctahedral smectite, partly based on thermodynamic estimation techniques (46, 53). Models are also included for some zeolites, based on similar methods (54).

Work is in progress to include site-mixing models in the forthcoming 3270 version. In site-mixing models, the ions are allowed to mix randomly on distinct kinds of sites, independently of the mixing on other kinds of sites. Molecular mixing is mathematically identical to site mixing over a single site, excluding mixing of vacancies. Both molecular- and site-mixing models can be treated as thermodynamically ideal or non-ideal, but there is little data in the 0-300°C temperature range to support the construction of non-ideal models. Work is presently focused on better models for smectites, illite, chlorite, and various zeolites. For example, to extend the compositional range of the smectite solid solution and to utilize a more appropriate model, an ideal site-mixing model for dioctahedral smectites (55) is being incorporated into EQ3/6.

An ion exchange approach is also being worked on. To allow reactant smectites and/or zeolites that are not in overall equilibrium with the solution phase to vary their exchange composition, fictive aqueous species, i.e. exchange 'complexes', are defined and used to model cation exchange (56). The form of the equilibrium relationship between exchange complexes and basis species determines the exchange convention, i.e. mole-fraction or equivalent fraction representation of ideal exchange. The association reactions are formulated to preserve equivalent fraction formalism because this is numerically equivalent to the treatment of exchange using ideal site-mixing.

Rate Laws. The principal kinetic rate laws included in the EQ6 code are the transition-state theory form (e.g., 28) and the Plummer et al. (32) rate law proposed for the dissolution and growth of carbonate minerals. Less important forms are discussed in ref. 25. Generally speaking, these models may include an implicit model of speciation on the surface of the dissolving or growing mineral. However, no explicit models for speciation on mineral surfaces are presently accounted for in EQ3/6. Further development of kinetics theory may require the inclusion of such models for coupling with future rate law models.

Redox Disequilibrium in the Aqueous Phase. Aqueous redox disequilibrium modeling is permitted in the 3245 version of EQ3NR, but not the corresponding version of EQ6. It will be permitted in the 3270 version of EQ6. This will allow, for example, calculation of seawater/basalt reaction models in which total sulfate is conserved instead of partially reduced to sulfide.

Numerical Methods and Data Structure. Both EQ3NR and EQ6 make extensive use of a combined method, using a "continued fraction" based "optimizer" algorithm, followed by the Newton-Raphson method, to make equilibrium calculations. The method uses a set of master or "basis" species to reduce the number of iteration variables. Mass action equations for the non-basis species are substituted into mass balance equations, each of which corresponds to a basis species.

In the 3245 version of EQ3/6, the Newton-Raphson algorithm was modified to treat activity coefficients of aqueous species as known constants during a Newton-Raphson step. The activity coefficients are adjusted by a "double update" method of back-substitution between such steps. This simplifies the coding of the Jacobian matrix and gives performance comparable to the older method in which these activity coefficients were adjusted along with other variables using a Ppure Newton-Raphson method.

The "double" update is employed to expand the description of the system from the new concentrations of the basis species because, strictly speaking, new values of the activity coefficients are also required to calculate new concentrations of the non-basis species, and vice versa. The code first recomputes the concentrations of dependent species using the old values of the activity coefficients, recomputes the activity coefficients, uses them to recompute the non-basis species, and recomputes the activity coefficients. The 3270 version will similarly treat the activity coefficients of species in solid solutions.

The operational basis set can be changed by a process known as "basis switching." Thus, a basis species which contributes little to a mass balance can be exchanged with a non-basis species, preferably one which dominates that balance. Such an operation tends to lead to improved numerical behavior. EQ3/6 has allowed users to specify basis switches on the input file. It has also had an option (not much used) to use basis switching as part of the "optimizer" to reduce the value of residuals prior to Newton-Raphson iteration. For version 3270, EQ6 will be modified to insure after each step of reaction progress that the basis set employed is the "best" one. Note that this adjustment will take place after Newton-Raphson iteration has converged. This change is being implemented to improve numerical behavior in calculations involving very large numbers of chemical components.

C.M. Bethke (57) has shown that significant numerical advantages in such calculations can be realized by switching into the basis set a mineral species that is in partial equilibrium with the aqueous phase. This avoids expansion of the size of the Jacobian matrix and reduces computation time. A method based on this concept is being developed for use in the 3270 version of EQ3/6. The concept appears to show promise for improvement of the "optimizer" algorithm as well as the Newton-Raphson one.

The data structure used in EQ6 through version 3245 did not permit implementation of these ideas. The basis set was defined as a subset of the aqueous species, so a mineral species could not be switched into the basis. The properties of the various types of species (aqueous, mineral, gas) were distributed over separate, analogous arrays. The old structure had also become inefficient in terms of storage when the data base became large. A new data structure is being implemented in EQ3/6 version 3270. This has a single list of species of all types. The basis set is defined by a pointer array. There is a single list of phases, and the species belonging to a given phase appear contiguously on the list of species. The arrays for stoichiometric composition and reaction coefficients have been restructured to eliminate the storage of many zero values. Parallel arrays define the elements or species that correspond to the coefficient values, and pointer arrays determine where in these arrays the entries for a given species begin and end.

Through version 3245, mass balances in EQ6 were defined by stoichiometric numbers based on elemental composition. In the 3270 version, they will be based upon reaction coefficients. To maintain a maximum degree of correspondence of mass balance totals defined in this manner with physically measurable quantities, the mass balances and associated stoichiometric factors will be defined and maintained in terms of the original (data file) basis set (or more strictly, the reactions written using this set).

An example shows how non-physical mass balances arise. Dissociation of the non-basis species $HgCl_3^-$ is written on the data file as $HgCl_3^- = Hg^{2+} + 3Cl^-$. Similarly, for $HgBr_3$, the reaction is written as $HgBr_3^- = Hg^{2+} + 3Br^-$. The mercuric, chloride, and bromide ions are all basis species. The stoichiometric relationships are all obvious; e.g., the mercuric trichloride complex carries a weight of three in calculating the total chloride. However, if this complex is switched into the basis set in place of mercuric ion, then the reaction for the dissociation of the bromide complex must be rewritten as $HgBr_3^- + 3Cl^- = HgCl_3^- + 3Br^-$. Looking only at the reaction coefficients, one would infer that this species carries a weight of -3 in the balance for chloride ion! Curiosities of this sort have routinely been dealt with in other modeling codes, such as Reed's codes (58) and MINTEQ (38). The totals are meaningful only in terms of the basis set employed. The only problem with the use of non-physical totals is that code users may confuse such quantities with those reported from chemical analysis. Except for three special cases discussed below, the procedure used in the new EQ3/6 code keeps the mass balance totals physically meaningful.

In the new code, the mass balance for water replaces one for elemental oxygen, the mass balance for hydrogen ion replaces one for elemental hydrogen, and the mass balance for oxygen gas replaces the charge balance. There is no general way to write the reactions to guarantee physical meaning to these new total quantities. The mass balance for water calculated by this method is generally numerically very nearly equal to the physical amount of water. However, in high pH solutions, a mass balance of hydrogen ion usually yields a negative number. In reducing solutions, the same sort of result is seen for oxygen gas. EQ3NR deals with these quantities only as calculated outputs, so their usage is significant primarily to EQ6. A principal advantage for EQ6 of redefining mass balances in this way is that the existing "continued fraction" based "optimizer" algorithm can be modified to apply to all the basis species; through version 3245, it could not be applied to these three special species.

Rate Law Integration. Kinetic rate laws are ordinary differential equations (ODEs) that are numerically integrated in EQ6 when such rate laws are invoked by the user. In version 3245, the method of integration is a simple "predictor" function modeled after the predictor-corrector method of Gear (59, 60). Integration accuracy is maintained by cutting the step size if an accuracy test is failed. In version 3270, a corrector function is being added to increase the robustness of the code. In version 3245, some problems have been observed to get caught running at small steps sizes for long periods of time due to the lack of an ODE corrector.

Current Directions in Using EQ3/6 in Geochemical Modeling

Current directions in code usage are illustrated by two examples, one dealing with pH buffers, the other with reaction of ground water with spent nuclear reactor fuel. The former case deals with small, relatively simple systems, the latter with a system that is about as large and complex as a geochemist is ever likely to see.

pH Buffer Calculations. Knauss and Wolery performed monomineralic dissolution rate experiments on albite (28) and quartz (29) in various pH buffer solutions at 70°C. The buffer compositions chosen were fairly standard ones taken from the literature (see ref. 28 for sources). The pH of these solutions was given for 25°C, not 70°C. It was necessary to obtain the values at the temperature of the experiments. This was done using the EQ3NR code. The method of calculation is illustrated for the case of the pH 4 buffer 0.05 *m* potassium hydrogen phthalate plus 0.0001 m HCl. The solution composition was constrained to satisfy 0.05 *m* total dissolved potassium, 0.05 *m* total dissolved phthalate, 0.0001 *m* total dissolved chloride. pH was input as 4.0 and the code was instructed to adjust the concentration of hydrogen ion as required to satisfy electrical balance. For a temperature of 25°C, the calculated pH was 4.00, in excellent agreement with expectations and close to a measured value of 4.06. For 70°C, the pH was calculated to be 4.11.

It was subsequently found that the high level of potassium in this buffer interfered with the measurement of dissolved sodium and aluminum in the albite experiments. Such high levels of buffering agent were not required to maintain the pH. In a subsequent study on the dissolution kinetics of muscovite (Knauss, K.G., and Wolery, T.J., Geochim. Cosmochim. Acta, in press), the concentrations of the buffering agents were reduced tenfold (e.g., the concentration of potassium hydrogen phthalate in the "pH 4" buffer was reduced from 0.05 m to 0.005 m). The code calculation was constrained to satisfy 0.005 m total dissolved potassium, 0.005 m dissolved phthalate, and pH 4.00 at 25°C. The total dissolved chloride was set to 0.0001 *m* and the code was instructed to adjust this to achieve electrical neutrality. The total dissolved chloride after adjustment was 0.0003 m, indicating that 0.0003 m HCl is required to make up the buffer. From this, the 70°C pH was calculated to be 4.06. The new buffer could as easily have been calculated to satisfy pH 4.00 at 70°C by, as before, adjusting the chloride to satisfy charge balance. This would have yielded a slightly different concentration of HCl in the buffer.

The use of EQ3NR to design custom pH buffer solutions represents a useful and one of the "safer" applications of EQ3/6. It is safer because there are no issues of kinetics or metastability to deal with. It is not absolutely safe, however, because the results do depend on the thermodynamic data used. On the other hand, many buffer compositions have been well studied and provide useful but limited tests of validation of the code and the thermodynamic data base.

Reaction of Spent Fuel and Groundwater. At the other extreme end of code usage is the work of Bruton and Shaw (19) to model reaction of spent nuclear fuel with ground water. These calculations include about forty chemical elements, employing almost the whole of the EQ3/6 thermodynamic data base. This modeling is currently only in the early stages, requiring a number of simplifying assumptions and proceeding in the likely absence of important thermodynamic data. Nevertheless, the modeling is proving useful in pushing for better characterization of experiments and in identifying thermodynamic data needs. A resonance between modeling and experimentation is expected to lead to models sufficiently dependable to make predictions of behavior of waste emplaced in the field.

One of the major outputs of these model simulations is a prediction of a sequence of secondary phases. These phases are important because they can act as sinks for radionuclides and other toxic components of the waste, limiting their migration away from the point of emplacement. Even phases not containing such components affect the overall course of reaction via effects on pH, redox conditions, etc. Figure 1 shows the results of one simulation for reaction of spent fuel and J-13 well water at 25°C. Haiweeite (a calcium uranyl silicate), soddyite (a uranyl silicate), and schoepite (a uranyl hydroxide) are successive (and overlapping) sinks for uranium, the dominant constituent of spent fuel.

The solubility constraints imposed by haiweeite and soddyite create an inverse relationship between dissolved silica and dissolved uranium. This is illustrated in Figure 2, which shows the evolution of total concentration of uranium, silica, and other selected elements. The silica in the system is essentially provided by the ground water. As reaction proceeds, uranium released by dissolution of the fuel is sequestered by silica into haiweeite. When a large fraction of the silica in the system is tied up in this phase, soddyite begins to form. In this phase, a given amount of silica can tie up more uranium than it can in haiweeite. The haiweeite redissolves as more soddyite forms. Finally, the released uranium has tied up nearly all the silica in the system in soddyite and the uranium concentration rises until it is limited by the precipitation of another uranium phase, schoepite, which contains no silica. The silica at the end of the reaction path is extensively tied up in the nickel silicate phase. The sequestering of uranium in uranyl silicates has been observed experimentally (see ref. 19), although uranophane, another uranyl silicate, is found instead of soddyite. Further work is planned to resolve this difference.

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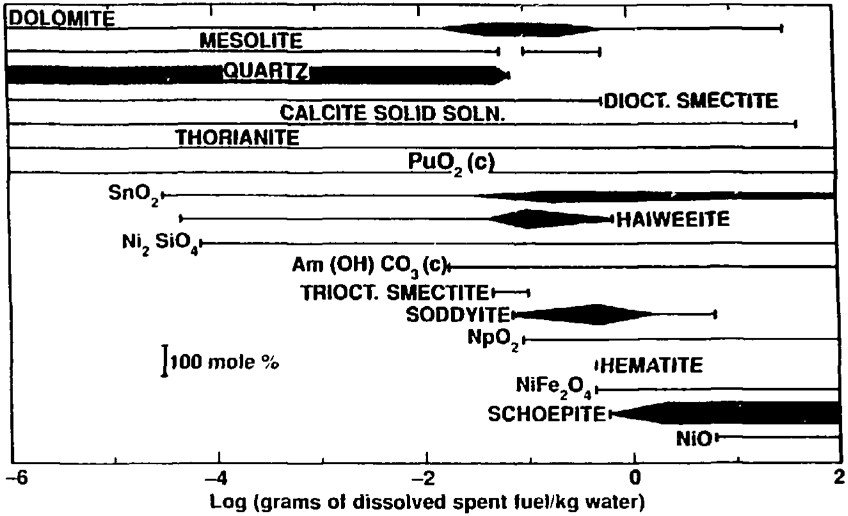
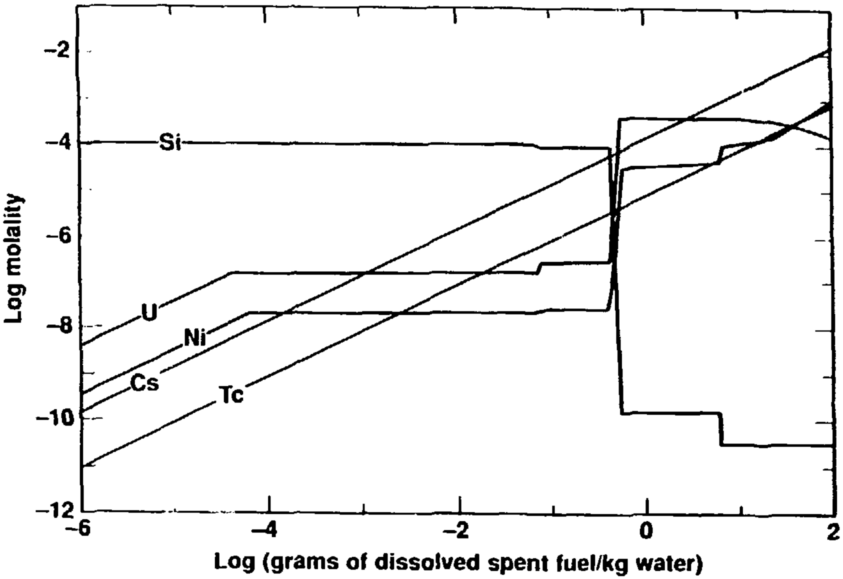
Figure 1. The predicted sequence of solid reaction products of reaction between spent nuclear fuel and J-13 well water at 25°C. The width of the bars represents the percentage of the number of moles of all precipitates at any given point of reaction progress. There is a break in the appearance of mesolite. There is no break in the appearance of $PuO_{2(c)}$. (Reproduced with permission from Ref. 19. Copyright 1988 Materials Research Society.)

Figure 2. The predicted concentrations of total dissolved Cs, Ni, Si, Tc, and U during the reaction of spent nuclear fuel and J-13 well water at 25°C . (Reproduced with permission from Ref. 19. Copyright 1988 Materials Research Society.)


DOLOMITE
MESOLITE
QUARTZ
DIOCT. SMECTITE
CALCITE SOLID SOLN.
THORIANITE
PuO2 (c)
SnO2
HAIWEEITE
Ni2 SiO4
Am (OH) CO3 (c)
TRIOCT. SMECTITE
SODDYITE
NpO2
100 mole %
HEMATITE
NiFe2O4
SCHOEPITE
NiO
–6
–4
–2
0
2
Log (grams of dissolved spent fuel/kg water)



−2
−4
−6
−8
−10
−12
Log molality
Si
U
Ni
Cs
Tc
−6
−4
−2
0
2
Log (grams of dissolved spent fuel/kg water)