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GEOCHEMICAL MODELS SUITABLE FOR PERFORMANCE ASSESSMENT OF NUCLEAR WASTE STORAGE: COMPARISON OF PHREEQE AND EZ3/EQ6, ONWI-473, INTERA ENVIRONMENTAL CONSULTANTS, HOUSTON, TX - (USED AS A REFERENCE IN OU 2 RI REPORT)

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Geochemical Models Suitable for Performance Assessment of Nuclear Waste Storage: Comparison of PHREEQE and EQ3/EQ6

Technical Report

June 1983

INTERA Environmental Consultants, Inc.
11999 Katy Freeway, Suite 610
Houston, Texas 77079

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ABSTRACT

Geochemical processes will significantly influence the performance of nuclear waste repositories. The computer codes EQ3/EQ6 and PHREEQE, can be used to describe these processes. They can be applied to far-field and near-field performance assessment and to evaluate data acquisition needs and test data. Both codes embody the ion- association conceptual model of solution behavior and can simulate geochemical reactions. The codes require thermodynamic data for each solid, gaseous or dissolved chemical species being modeled. The data bases accompanying the codes are for testing purposes only and should not be applied to real problems without first being carefully examined. Five test problems have been run for code verification and demonstration. Routines to manipulate thermodynamic data were written so that each code could run with both data sets. Two problems of aqueous speciation in sea water verified the codes by comparison of results with hand calculations and illustrated the extent of the test data bases supplied. The third problem simulated the dissolution of microcline and verified both codes' ability to locate phase boundaries and simulate non-redox reaction paths. The fourth problem verified the codes' ability to follow abrupt redox changes in a reaction path simulation, while the fifth tested the temperature changing capacity of the codes. When run with the same thermodynamic data, each code gave virtually identical results in all problems.

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1 INTRODUCTION

The initial major task of the SCEPTER (Systematic Comprehensive Evaluation of the Performance and Total Effectiveness of Repositories) Program being carried out by INTERA for ONWI is to assemble a tested and useful set of computer models suitable for nuclear waste performance assessment. Geochemical processes will have a profound influence on the behavior of nuclear waste sites, repositories and waste packages, and so methodology to quantitatively estimate the extent of geochemical effects on their performance are necessary. We have therefore, carefully reviewed the literature describing the present state-of- the-art of geochemical modeling and from the rather large number of such models which have been described, have selected two for detailed in-house testing. The selected codes are PHREEQE (Parkhurst, Thorstenson, and Plummer, 1980, 12 January 1981 version) and the EQ3/EQ6 package (Wolery, 1979, EQ3.3015U19, 9 APRIL 1981 and EQ6.3015U93, 28 MARCH 1981 versions). The features of these codes which led to their selection include the generality of the coded algorithms, the non-proprietary nature of the codes and their general availability, the fact that they are easily portable from one computation system to another, their operating efficiency and the fact that they include the capability, at least in principle, to handle such important but difficult geologic processes as chemical kinetics and solid solutions.

In this report we present a brief description of the theory on which the geochemical models are based, plus a brief discussion of how this theory is transformed for practical operation in the codes selected. We then present a comparison between the results of operating the two codes on a series of test problems. By operating both codes on the same set of problems, and finding comparable results, we have verified the code construction by a code to code comparison test. These problems were chosen to demonstrate the abilities of these codes to handle various types of geochemical processes including speciation of complicated solutions, phase boundary location and changing temperatures. Though these problems

do not specifically illustrate waste isolation systems, the processes they describe will certainly be important influences on the behavior of such systems. It is important to note, though, that there is no intention that this report be an operating manual for either of the codes.

Finally, we point out areas of strengths and weakness in our present ability to assess the probable effects of geochemical processes on repository performance. The major weaknesses, most of which have been pointed out by others, include the inapplicability of the aqueous model contained in any of the available computer codes to waters of high ionic strengths, such as are likely to be found in salt repositories; the spotty availability of the thermochemical data needed for aqueous speciation and solid-solution equilibria, particularly among actinide elements; the almost total absence of data on the kinetics of mineral precipitation and dissolution; and the limited ability of present models to handle mineral solid solutions and mineral reaction kinetics even were more data on these processes available.

The documentation for the geochemical codes PHREEQE and EQ3/EQ6 appears in separate reports (INTERA, 1982 a and b). The documentation for the thermodynamic data routines EQTL, PHTL, and PQTL, referred to in section 4 below, which were adapted or written for this code comparison report also appears in these two reports.

1.1 APPLICATIONS OF GEOCHEMICAL MODELS

This section does not attempt to present an exhaustive list of geochemical questions which may come up during the course of repository performance assessment, because such questions are discussed by Moody (1982) and INTERA (1981), for example. Instead, it discusses selected examples of the types of applications expected of geochemical models. The examples fall in the categories of near-field and far-field performance assessment and of the evaluation of data acquisition needs and test data.

1.1.1 Far Field Performance Assessment

Far field performance assessment focuses on the ground-water transport of radionuclides and uses models which simulate retardation of nuclides resulting from geochemical reactions between the moving solution and stationary aquifer framework (Pearson, 1981).

The extent of retardation of a substance can be expressed in terms of its partitioning between the moving fluid and stationary solid phases. That is:

$$R_{\underline{i}} = \frac{V_F}{V_{\underline{i}}} = \frac{M_{T,\underline{i}}}{M_{F,\underline{i}}} = 1 + \frac{M_{S,\underline{i}}}{M_{F,\underline{i}}} = 1 + k_{M,\underline{i}} \qquad (1.1.1)$$

where:

R = retardation coefficient,

V = velocity,

M = mass,

k_M = mass partition coefficient,

and the subscripts:

F refers to the fluid phase,

S refers to the solid phase,

T is the total, e.g. $M_T = M_F + M_S$, and

$\underline{i}$ refers to the species (element or nuclide) of interest.

In most transport models, the solid-solution interaction described by $k_{M,\underline{i}}$ is assumed to result from sorption behavior and described by a simple linear isotherm. While such isotherms fit a number of experimental data sets, the actual chemical process operating may be more than simple sorption (Veith and Sposito, 1977). In fact, the value of the mass partition coefficient will be determined by all of the chemical reactions which occur between the fluid and solid phases and among the several solid phases themselves. Reactions such as solution/precipitation, ion exchange, hydrolysis and solution complexing, oxidation/reduction, simple sorption, and others will act together to set mass partition coefficient values. A

need for geochemical modeling in far-field performance assessment is to simulate these reactions and realistically evaluate the mass partition coefficients required for transport calculations.

1.1.2 Near-Field Performance Assessment

Near-field concerns embrace both the repository and the waste package. To model nuclide transport by ground water within the repository region will require the same sort of geochemical modeling to evaluate mass partition coefficients that will be done for far-field. Near-field requirements for this type of geochemical modeling will be more stringent than the far-field requirements because thermal effects will be more important in the vicinity of the repository than in the far-field (INTERA, 1981).

The performance of the waste package will be particularly influenced by geochemical considerations. In concept, the waste package will consist of a waste form encased in a canister surrounded by back-fill. Before a radionuclide in the waste form can reach the repository, it is necessary that:

- The canister be corroded - a process with rate strongly dependent on the chemistry of the corroding fluid;
- The nuclide leach from the waste form - where the rate of leaching has a complex dependence on the geochemistry of the leaching fluid;
- The nuclide traverse the back-fill to the repository boundary - the rate of which transit will be very strongly influenced by reactions between the nuclide in solution and the chemically highly reactive material which may be used for back-fill.

Geochemical modeling is needed to provide the boundary conditions for adequate waste package performance assessment as well as for the modeling of nuclide transport within the repository. A number of recent reports, such as those by Deutsch (1980) and Smith (1980), discuss the application of geochemical models to near-field problems.

1.1.3 Data Acquisition Needs and Test Data Evaluation

In addition to their importance in performance assessment, geochemical models are needed to guide data acquisition activities (INTERA, 1981; Jenne, 1981). Such models when used in a sensitivity analysis mode will help set priorities and help specify the precision needed in the laboratory collection of thermodynamic and kinetic data. Such model usage will also guide field data collection activities by helping to select from several potentially measurable parameters the one which will be of most use for performance assessment purposes.

A second broad use of geochemical models will be to assist in the interpretation of data collected as part of specific site evaluations. Interpretation of such data in terms of, for example, the mineralogical controls on the chemistry of ground water will be important in defining the state of the system on which effects due to waste emplacement will be superimposed. The use of models to interpret regional aquifer geochemistry is exemplified by a number of recent reports, of which that by Thorstenson, Fisher, and Croft (1979) can be cited.

1.2 OVERVIEW OF GEOCHEMICAL MODELS

Although geochemical models are being used with increasing frequency, their principles of operation and mode of application may still be unfamiliar to many people active in waste repository performance evaluation. Thus, before describing PHREEQE and EQ3/EQ6 and the detailed results of the intercomparison between them, it is appropriate to briefly describe the nature and use of geochemical models and to mention several of the detailed published reviews of such models which have recently appeared.

1.2.1 Geochemical Model Types

The two types of geochemical models can be termed aqueous solution models and geochemical reaction models.

Aqueous solution models are used to calculate such thermodynamically important quantities as free ion activities from measured chemical compositions of solutions. The quantity which determines whether a mineral will dissolve or precipitate, or which effects the rate of leaching from a waste form near equilibrium, is not the total concentration of the element or nuclide in the solution, but its thermodynamic activity. Both laboratory and field measurements however, tend to be only of total elemental concentrations. Models which calculate thermodynamic activities from measured concentrations are called "aqueous solution" or "aqueous speciation" models.

Geochemical reaction models describe changes in the chemistry of solutions and associated solids which occur as reactions proceed. Such reactions may be brought about by mixing two solutions, adding solid material to a solution, or by changing the temperature of a solution or a solution and solid. Geochemical reaction models describe the behavior of such reacting systems in terms of the masses of elements which are transferred between solid phases and the solution or from one solid to another.

Geochemical reaction models may simulate reaction paths or simply calculate mass transfer. A reaction path model describes the evolution of the system as it reacts from a given fluid and solid composition to a final state in which all solids and the fluid are in thermodynamic equilibrium. The model itself calculates the identities of the phases which precipitate or dissolve as a reaction progresses and calculates their amounts and the resulting changes in solution composition. Reaction path models are required to take very small steps of reaction progress in the vicinity of phase boundaries, and have extensive computer core and time requirements.

Mass transfer models, on the other hand, calculate masses of phases dissolved or precipitated and the associated fluid compositions resulting from user specified reaction steps and phase assemblages. While these models require considerably greater user knowledge of the system being modeled than do reaction path models, they are computationally considerably more efficient.

Both PHREEQE and EQ3 include aqueous speciation models based on the same chemical principles. The techniques used to solve the resulting equations are different in the two codes, however, with the PHREEQE algorithm being computationally more efficient than that included in EQ3. EQ6 is a reaction path model which begins its simulation with the solution specified by the results of an EQ3 run. PHREEQE includes mass transfer calculation capability.

1.2.2 Recent Reviews and Summaries

Computer models have been used to perform calculations of interest in the field of aqueous geochemistry since the late 1960's but the use of such models became common only in the late 1970's. Many of the most frequently used and mentioned aqueous solution models were reviewed and compared by Nordstrom and others, 1979.

Only rarely is a complex computer model of any process developed entirely from first principles with no reference to similar preceding codes. Geochemical codes obey this precept and thus, a brief description of the historical evolution of certain of the major groups of codes is useful as a means of distinguishing among the large number of named codes which exist today.

There are two major lines of codes which perform aqueous speciation calculations which Nordstrom and others (1979), term the Newton-Raphson Programs and the Successive Approximation Programs. The first in the series of Newton-Raphson Programs is known as REDEQL and was developed and first described by Morel and Morgan (1972). In addition to solving for aqueous speciation, REDEQL like EQ3, has the capacity to calculate the concentration of a dissolved element or elements based on user specified mineral saturation constraints. Other more recent codes developed from the principles established in REDEQL include REDEQL2, MINEQL, and GEOCHEM, references to which are given by Nordstrom and others (1979). Although codes of this type are widely used, they have no features which are not duplicated in PHREEQE and/or EQ3/EQ6. Thus, in order to keep the number of codes adopted in the SCEPTER Package to the minimum required, no codes from this group were adopted.

The Successive Approximations approach to calculating aqueous speciation was used by Garrels and Thompson (1962) in their pioneering manual calculation of the distribution of dissolved species in sea-water. The earliest well-known general solution codes developed following this principle were WATEQ (Truesdell and Jones, 1973) and SOLMNEQ (Kharaka and Barnes, 1973). Table 1-1 lists a number of the Successive Approximation codes and references to them. These include a FORTRAN version of WATEQ called WATEQF as well as several modified PL/1 versions: WATEQ2 and WATEQ3.

While the WATEQ series of codes, as well as SOLMNEO and its descendants, are well-known and widely used, they have a serious disadvantage as compared to the aqueous speciation portions of PHREEQE and EQ3. Their disadvantage is that each reaction considered by them requires a separate line of code in the program itself. Thus, to change the identities or compositions of individual aqueous species or minerals requires a change in the programs themselves. This need for change has given rise to a succession of named codes (WATEQ3, for example), which differ from their predecessors (WATEQ2 in this case) only by their inclusion of additional aqueous species and mineral reactions.

In contrast, the aqueous models included in PHREEQE and EQ3 are general in that the coded algorithm does not refer to specific elements or species, ion pairs or minerals. Instead, in these codes the identities of the chemical species to be included and the reactions among them are entered as data to the program and the program itself need not be changed to accommodate different solution species, elements, or minerals.

PHREEQE can only loosely be considered a descendant of the WATEQ series of codes because, while it does use a continued fraction version of the Successive Approximations approach to the solution of the chemical speciation model, its generally coded algorithm and ability to calculate mass transfer set it apart from the WATEQ group. Similarly, EQ3 although it performs functions of an earlier routine called SOLSAT (part of PATHI), does so by means of a monotone sequence approach to the Successive Approximations. This and other differences are significant enough that EQ3 also can be considered only very loosely as a descendant of preceding codes.

Table 1-1 Geochemical Programs Frequently Referred to in this Report, with Primary References and Programming Language. Additional Geochemical Solution Programs are Listed with References by Nordstrom and Others, 1979.

PROGRAM NAME	REFERENCE(S)	PROGRAMMING LANGUAGE
EQ3/EQ6	Wolery and Walters, 1975 Wolery, 1979	FORTRAN
MIX2	Plummer, Parkhurst, and Kosiur, 1975	FORTRAN
PATHI	Helgeson and others, 1970	FORTRAN
PHREEQE	Parkhurst, Thorstenson and Plummer, 1980	FORTRAN
SOLMNEQ	Kharaka and Barnes, 1973	PL/1
WATEQ	Truesdell and Jones, 1973, 1974	PL/1
WATEQF	Plummer, Jones and Truesdell, 1976	FORTRAN
WATEQ2	Ball, Jenne, and Nordstrom, 1979	PL/1
WATEQ3	Ball, Jenne, and Cantrell, 1981	PL/1

Although a number of aqueous speciation codes have been written, very few mass transfer or reaction path modeling programs existed prior to EQ3/EQ6 and PHREEQE. The first reaction path code, called PATHI, was developed by Helgeson in the late 1960's and expanded by Helgeson and his students during the succeeding decade. PATHI, although successful in simulating irreversible reactions between solutions and solid phases, was computationally inefficient and tended to drift away from the governing algebraic constraints of mass and charge balance and mass action. This drift occurred because the code integrated the differential counterparts of the governing equations by evaluating truncated Taylor's series.

The EQ6 code performs all the functions of the original PATHI code but is computationally considerably more efficient, and because it corrects finite-difference approximations to the PATHI Taylor's series to satisfy the original algebraic constraints, does not suffer from the potential numerical error difficulties of the earlier code. EQ6, therefore, was adopted as the general reaction path code for this work.

PHREEQE is capable of calculating the amount of mass transfer required for a given solution to reach equilibrium with specified mineral phases. A predecessor code, MIX2, also calculated mass transfer amounts but was limited to simple carbonate-sulfate systems and did not consider oxidation-reduction reactions. PHREEQE also is capable of calculating reaction paths, but only given input on the phase boundaries along them. The solution algorithm in PHREEQE is extremely efficient however, and as phase boundary locations and the mass transfer required to reach them are frequently of importance in repository assessment calculations, PHREEQE has been adopted with EQ6.

2 CONCEPTUAL BASIS OF GEOCHEMICAL MODELS

The term "model" is often used in place of "code" to refer to a computer program which is used to simulate the behavior of some process. It is important to make clear the distinction between the physical description of the system which has been chosen and the method by which that description is used for practical calculations. The description of the system - the group of principles which govern the behavior of the system - is here called the conceptual model and is to be distinguished from PHREEQE or EQ3 which are names of computer programs or codes by which the principles embodied in the conceptual model are applied to practical problems.

2.1 AQUEOUS SOLUTION MODELS

The conceptual model most often applied to aqueous solutions in geochemistry is the ion-association or ion-complexing model, originally due to Bjerrum. This model assumes that oppositely charged dissolved ions react to form complexes which are treated as thermodynamic entities. These complexes are assumed to be in equilibrium with the free ions and the equilibria described by thermodynamic equilibrium constants.

The popularity of this approach in geochemistry stems from its early use by Garrels and Thompson (1962) to interpret the chemistry of sea water, and its inclusion in the first-generation computer programs WATEQ, SOLMNEQ, and others constructed for the interpretation of aqueous solutions.

A point which has favored the continued use of the ion-association model is that there exist for it many suitable thermodynamic data. These data result from the fact that such a model is frequently used to reduce laboratory experiments on solution behavior. Data so treated are, in turn, suitable for the model to use. In spite of the wide availability of data, problems frequently occur which cannot be handled satisfactorily because data needed specifically for them

or for particular elements important to them are not available. The data needs of PHREEQE and EQ3/EQ6 are discussed with the test problem descriptions in Chapter 4.

The most serious limitation to the ion-association model presently available is that it becomes less capable of representing real solution behavior as the salinity of the solution increases. In general, this model behaves well in solutions with salt contents as high as one molal, certainly including the range of normal sea water which is 0.7 molal. At concentrations significantly greater (a few molal) and particularly in such highly saline waters as brines, the ion-association model breaks down.

A second conceptual solution model, the mixed electrolyte model, is beginning to come into use in geochemistry. This model does not assume the existence of explicitly defined complex ions in solution as does the ion-association model but, instead, uses an expression for the activity coefficient of ions as functions of the concentrations of all ions in solution. The formalism for this conceptual model is presented by Pitzer (1973) for single electrolyte solutions and by Reilly and others (1971), and Pitzer and Kim (1974) for mixed electrolytes.

The mixed electrolyte conceptual model is advantageous in that it is able to reproduce the properties of solutions at all concentrations, including those far more saline than could be satisfactorily treated using the ion-association model. This has been demonstrated in recent work by Eugster and others (1980) who use a model described by Harvie and Weare (1980) to simulate the sequence of minerals which deposit from evaporating sea-water. Because extremely good experimental data are available on this mineral sequence, Eugster and others can be considered to have validated mixed electrolyte models for geochemical problems in highly saline solutions by successfully simulating this sequence.

In spite of the fact that saline solutions such as those associated with salt deposits may be of importance in certain nuclear waste repository analyses, no mixed electrolyte model is included in the SCEPTER Package at this time for two reasons. First, no generally

available code exists which makes use of the mixed electrolyte conceptual model in its aqueous speciation routine. The Harvie and Weare (1980) code, for example, has not been published. Second, only limited experimental data are available to evaluate the coefficients which occur in the activity coefficient expressions used in this model. Most of these data are restricted to simple solutions containing salts of Na^+, K^+, Ca^{+2}, Mg^{+2}, SO_4^{-2}, and Cl^- which, while appropriate for examining evaporating sea-water, are of less utility for examining the behavior of radionuclides of exotic chemical elements. In addition, only recently have data at temperatures other than 25 C begun to be available (see, for example, Peiper and Pitzer, 1981). Given this lack of data for real systems of interest to performance assessment and the lack of a readily available mixed electrolyte model elsewhere, it was decided that the development of a mixed electrolyte model for inclusion in the SCEPTER Package would be inappropriate at this time.

The remainder of this section is concerned with a general description of the equations by which the ion-association aqueous solution model is described. The methods by which PHREEQE and EQ3 solve these equations and their auxiliaries also is outlined. No attempt has been made here to be entirely rigorous in the description either of the aqueous solution model equations or their programmed solutions, but only to convey generally what the programs do, and why. For details, the reader should consult the code documentation (INTERA, 1982a, b) and the descriptions of the programs given by their authors (Parkhurst, Thorstenson, and Plummer, 1980; Wolery and Walters, 1975; and Wolery, 1979).

2.1.1 Governing Equations

Information available on a solution usually comprises concentrations of dissolved elements. Although analytical data commonly refer to total concentrations, in the actual solution, according to the ion-association model, the element is present not only in its free form but also paired with other species.

To describe real solutions using the ion-association model one first writes a mass balance equation for each element, i, for which analytical data are given:

$$m_{T,i} = m_i + \sum_{j=1}^{J} n_{ij} m_j, \quad i = 1, 2, \ldots, I \qquad (2.1.1)$$

where: m_i = concentration of free element of species i;

m_j = concentration of complex ion j containing n_{ij} moles of i;

$m_{T,i}$ = total (analyzed) concentration of i;

I = total number of elements for which analytical data are available or which are being considered; and

J = total number of solution complexes. (If the complex j does not include element i, n_{ij} is zero).

The complex ions themselves are entities which have equilibrium concentrations described by mass action equations:

$$a_j = K_j \prod_{i=1}^{I} a_i^{n_{ij}}, \quad j = 1, 2, \ldots, J \qquad (2.1.2)$$

where: a_j = thermodynamic activity of solution complex j;

a_i = thermodynamic activity of free elements, i;

n_{ij} = stoichiometric coefficient of ion i in species j;

K_j = equilibrium constant for formation of complex j; and

I and J are as for equation 2.1.1.

The solution activities, a, in terms of which equations (2.1.2) are written, are related to the concentrations, m, of equation (2.1.1) by:

$$a_i = \gamma_i m_i \qquad (2.1.3)$$

in which γ is the activity coefficient. Activity coefficient values for each species depend on temperature, pressure, and the concentrations of all other species in the solution. A number of methods for calculating activity coefficients have been proposed. Those incorporated in PHREEQE and EQ3/EQ6 are discussed in Section 3.2, below.

Equilibrium constants are functions of temperature and pressure, and the values required for each of the J equations (2.1.2) will be part of the thermodynamic data base required for the problem. Further, I total concentration values from chemical analyses will be available. Even with equations (2.1.3) relating a and m values, two additional phenomena must be accounted for before the sets of equations (2.1.1) and (2.1.2) can be solved.

The first additional requirement is to account for the involvement of the ions H^+ and OH^- from the solvent itself in some of the solution complexing reactions. While the activities of the two ions are related by a mass action expression for water,

$$a_{H_2O} = K_w \; a_{H^+} \; a_{OH^-}, \qquad (2.1.4)$$

either an additional equation or an additional specified input parameter is still needed.

Programs of the WATEQ/SOLMNEQ group require that pH (= $-\log a_{H^+}$) be entered, eliminating the need for an additional equation. In MIX2, which was derived from WATEQF, the need for a specified, fixed pH was eliminated by making use of the fact that a solution can have no net electrical charge. This <u>electro-neutrality</u> principle is embodied in the equation:

$$0 = \sum_{i=1}^{I} m_i z_i + \sum_{j=1}^{J} m_j z_j \qquad (2.1.5)$$

where z is the charge on the dissolved species and the sums are over all I+J dissolved ions.

If, on the other hand, pH is specified, a net charge can be calculated. The departure of this net charge from its theoretical value of zero is a measure of the adequacy of the analytical data entered.

The calculation of aqueous solution speciations in both PHREEQE and EQ3 permit either the entry of pH or its calculation from the electroneutrality equation.

One last phenomenon must be accounted for to completely pose the aqueous solution problem. This involves the manner in which oxidation-reduction (redox) reactions are treated. One approach is simply to ignore redox reactions by writing separate mass balance equations (2.1.1) for each oxidation state of an element, and entering corresponding total concentration values. For a solution containing iron, for example, separate equations for Fe^{+2} and Fe^{+3} would appear, and two total concentration values (m_T, Fe^{+2} and m_T, Fe^{+3}) would be required.

A second alternative is to treat all oxidation states of an element as products of reactions of a single chosen state of the element. For iron, for example, Fe^{+2} might be chosen as the species in terms of which the mass balance equation (2.1.1) would be written. Fe^{+3} and its complexes then simply become members of the sum in the mass balance equation. An additional mass action expression is also added for the reaction by which the two oxidation states are related.

Mass action expressions for this or for any other redox reaction require a definition of the oxidation potential of the solution. This is accomplished by requiring that the value of the oxidation potentials be part of the solution definition data entered if redox couples are to be considered. PHREEQE requires that pe be entered. ($pe = -\log a_{e^-} = 16.90*Eh$ (volts) at 25 C). The oxidation potential for EQ3 can be defined by entering pe, Eh (volts), the fugacity of oxygen, or by specifying a redox couple for which both oxidized and reduced species concentrations will be entered and used to calculate the oxidation potential of the solution. All of these options amount to the same thing: if oxidation-reduction reactions are to be considered, an additional piece of input data is required.

The unknowns, equations, and data needs to solve an aqueous solution model can be summarized as follows: In a solution of I solute elements capable of forming J complexes, the I + J values of free and complex ion concentrations (or activities) are to be found, along with the two concentrations (or activities) needed for the solvent, and the E species which are oxidation or reduction products of the species representing the element. Thus there are I+J+E+2 unknowns.

To set against these are I mass balance equations, J complex association reactions, E redox reactions and the dissociation of water mass action equations - a total of I+J+E+1 equations. The extra one unknown is handled either by specifying pH, and so reducing the unknowns by one, or by adding the electoneutrality requirement and so increasing the equations by one.

Data required are I values of total dissolved elemental concentration, J complex ion association and E redox reaction equilibrium constant values, a value for the oxidation state of the initial solution, and, if the electroneutrality equation is not included, the pH of the solution.

Two approaches have been taken to the solution of the set of equations specifying the aqueous model. The method of successive approximations was used by Garrels and Thompson (1962) in their pioneering hand calculation of the distribution of aqueous species in sea water. This method is illustrated in the discussion accompanying test problem 1 below.

The successive approximations approach was adopted in a number of the early aqueous speciation programs including WATEQ and SOLMNEQ and it is used as well in PHREEQE and EQ3. It was used in the early WATEQ and SOLMNEQ codes in what Wigley (1977) referred to as a "brute force" method. In this method, the mass action expressions (2.1.2) are substituted into the mass balance equations (2.1.1) and the result solved directly for free element concentrations. Iteration through the system of equations continues with the results of the previous iteration being used as the starting estimate for the present iteration. When the calculated total concentration of each species agrees with the input concentrations within some user set tolerance, the system is considered solved.

Wigley (1977) pointed out that the combined mass balance, mass action equation can be rewritten in the form of a continued fraction which converges with many fewer iterations than are required by the brute force method. The continued fractions approach to successive approximations is adopted in WATEQF and is used to solve the mass balance equations (2.1.1) in PHREEQE. Wolery and Walters (1975) have described a monotone sequence method of controlling the continued

fraction series in the method of successive approximations. This has the advantage of increasing stability with respect to a wide range of input aqueous solution compositions and has been adopted in EQ3.

The second general approach taken to the solution of aqueous speciation equations makes use of the Newton-Raphson technique. Morel and Morgan (1972) used this method in their aqueous speciation program REDEQL and the method has been retained in the various other aqueous speciation codes derived from the Morel and Morgan program. The Newton-Raphson approach is also used in PHREEQE for the solution of all equations other than the mass balance equations for which, as mentioned above, a continued fraction approach to the method of successive approximations is employed.

The WATEQ/SOLMNEQ group of codes provide a thermodynamically adequate description of the solution given analyzed total elemental concentration data. Further, they use this calculated solution description to determine the affinities of various reactions which the solution could undergo. These codes do not actually calculate affinities, but rather, the Saturation Index (SI) which is related to the thermodynamic affinity (A) by the expression:

$$A_{\underline{p}} = -R*T*2.303*SI_{\underline{p}} \qquad (2.1.6)$$

where

$A_{\underline{p}}$ = Thermodynamic affinity (Joules/mole)

R = Gas constant (8.3143 Joules/mole-Kelvin)

T = Temperature (Kelvin)

$SI_{\underline{p}}$ = Saturation index for phase $\underline{p}$ as defined in equation (2.1.8) (dimensionless)

2.303 = ln 10

The calculated aqueous species activities are used to calculate reaction quotients for minerals with which the solution could potentially react. Reaction quotients (Q) which are also frequently called ion activity products (IAP), are equivalent in form to mineral equilibrium constants (K). That is:

$$Q_{\underline{p}} = IAP_{\underline{p}} = \pi_{\underline{i}} \; a_{\underline{i}}^{n_{\underline{ip}}} \qquad (2.1.7)$$

The tendency for a mineral, p, to dissolve in or precipitate from a solution is indicated by comparing the IAP and K using the saturation index:

$$SI_{p} = \log \frac{IAP_{p}}{K_{p}} \qquad (2.1.8)$$

If SI = 0, the mineral and solution are at equilibrium; if SI > 0, the mineral will tend to precipitate from the solution while if SI < 0, the mineral will tend to dissolve.

The most important use of the WATEQ/SOLMNEQ family of codes has been to calculate mineral saturation indices for natural water samples. These saturation indices can then be compared with the mineralogy of the aquifer from which the sample was taken and used to assess the validity of hypotheses concerning the identity of minerals presumed to be dissolving or precipitating and so controlling the observed water chemistry.

2.2 GEOCHEMICAL REACTION MODELS

The aqueous speciation models just described are static in the sense that while they calculate the aqueous speciation existing in a given solution as well as the tendency of minerals to dissolve or precipitate in the solution, they do not calculate the changes in mineral quantities and solution compositions which would occur as the solution reacts toward equilibrium. Calculations of this type are particularly important to repository performance assessment. While WATEQ type models are useful for testing hypotheses regarding mineral reactions which may have led to an observed water concentration, they cannot be used in a predictive mode to estimate changes in the geochemistry of waters and their containing rocks brought about by the introduction of waste.

Both the PHREEQE and EQ3/EQ6 codes described here and adopted in the SCEPTER Package, are able to perform all the aqueous speciation modeling functions of the WATEQ/SOLMNEQ group of codes, but in addition, are able to describe quantitatively the effects of ongoing geo-

chemical reactions. They do this by describing the changes in solution composition and in relative masses of solids which occur as a system comprising solids, gases, and a solution reacts toward a new equilibrium state following a perturbation. The system description given by these models is in terms of the masses of material transformed from phase to phase during the course of the reaction. They are thus known as mass transfer or as reaction path models.

Two approaches have been taken toward the development of geochemical reaction models. The approach realized in PHREEQE is that of mass transfer modeling in which the code solves directly for the final equilibrium state of a system given a series of initial conditions. In EQ6 on the other hand, the reaction path approach is used in which small steps of reaction progress are taken from an initial state toward equilibrium and the entire reaction path from initial to final state is calculated and displayed rather than simply the mass transfer involved in the overall reaction from the initial to the final state.

2.2.1 Mass Transfer Models

Mass transfer models are similar to the aqueous speciation models in that they assume a state of equilibrium throughout the entire system of interest. That is, they assume that not only do the aqueous phase reactions occur rapidly, but also that all potential solid phase dissolution or precipitation reactions occur equally rapidly.

Solution reactions with solid or gas phases are handled in much the same way as are ion complexation reactions in the solution itself. For each mineral or gas reacting, a mass action expression can be written similar to equation (2.1.2):

$$K_p = \pi_i \; a_{ip}^{n_i}, \qquad p = 1, 2, \ldots, P \qquad (2.1.9)$$

where

a_i = activities of dissolved free ions i;

K_p = equilibrium constant for the dissolution of phase p;

n_{ip} = stoichiometric coefficient of ion i in phase p.

The addition of this equation to the set of equations describing the system allows the addition of another unknown to the mass balance equations for each ion i. This additional term is simply the number of moles of i which must be transferred between the solution and the phase p to bring the system to equilibrium.

The direct mass transfer code PHREEQE has been included in the SCEPTER Package for several reasons. First, by virtue of its structure, it tends to run rapidly and efficiently and therefore can be used at little cost. It is valuable for performing calculations in rapidly reacting systems such as solution mixing problems and solution reaction with minerals that are likely to dissolve or precipitate rapidly. It is also useful for long time scale problems and for boundary calculations where system equilibrium is a reasonable boundary state.

PHREEQE will also calculate changes in solution composition with specified mass transfers into or out of the system. Thus the code can be used to simulate the path followed by a system reaching irreversibly with a solid or another solution.

2.2.2 Reaction Path Models

The reaction path simulation code E06 is also included in the SCEPTER Package. In this code, as in other reaction path models, it is assumed that equilibrium exists within the solution and between the solution and reaction product phases. During a reaction, equilibrium will persist among dissolved species, and further, if the solution becomes oversaturated with respect to a phase, that phase will immediately form in whatever quantity is required to return the solution to equilibrium. The particular value of this approach to repository performance assessment (Wolery, 1980) is that it permits the

simulation of the path by which a system originally at dis-equilibrium reacts toward equilibrium. Information from this path simulation includes the masses of solid phases dissolved or formed during the course of the reaction including transient phases, rather than simply the overall mass transfer required to go from the initial to the final equilibrium state.

Reaction path models are based on the principles of irreversible or non-equilibrium thermodynamics. The development of the equations by which these principles are applied to geochemical problems is due to Helgeson (1969) and his students (Helgeson and others, 1970). The application of these principles within the EQ6 code is described in detail by Wolery (1979).

Basically, Helgeson's approach consists of differentiating equations describing the reaction to be tracked with respect to a reaction progress variable. The progress variables measures the extent of reaction of a set of irreversible reactions which proceed according to specified relative reaction rates. The series of differential equations, together with the mass action and mass balance equations necessary to describe the equilibrium within the fluid phase, are sufficient to define the problem and in principle, can be solved for the amount of mass transferred at any stage of reaction progress.

The original computer code embodying Helgeson's approach was called PATHI or PATHCALC (Helgeson and others, 1970). In this code the differential equations describing mass transfer were solved by a truncated Taylor's series technique. An aqueous speciation model first produced a description of the initial solution and calculated the affinities with respect to possible products of reaction between the solution and existing specified phases. Then small arbitrary steps in reaction progress were taken in the direction of reducing these affinities. Numerically, the first and second derivatives of system parameters were found by solving a set of linear differential equations, which were then used in a truncated Taylor's series. Following each step of reaction progress the new solution was resolved and affinities calculated again. When phase boundaries were reached (when the affinity of any reaction became zero or negative)

a process of interval-halving was used to more precisely define the exact value of the reaction progress variable at equilibrium between the solution and that phase.

Obviously such a solution procedure is very slow to compute and furthermore, has a tendency to drift because of the truncation. So, after many steps of reaction progress, such a model tends to produce system compositions different from those which would result from a one-step mass transfer calculation.

In order to reduce the computer time required for simulations using PATHI, high-order predictor-corrector methods of integration were put into a version of the program developed at Los Alamos Scientific Laboratory (Herrick, written communication 1976, reported by Wolery, 1979). Programs of this type are presently in use by several investigators. This modification improves the running speed of the program markedly and it diminishes, but does not eliminate, the problems of drift.

Another approach to the solution of reaction path computations was taken by Wolery (1979) in EQ6. This program is a combination of the direct mass transfer approach of the previous section with the differential path-following concept of PATHI. While reaction paths continue to be predicted by finite-difference approximations to Helgeson's Taylor's series, the compositions at points are re- calculated directly by applying a mass transfer approach like that described in the previous section. Any drift introduced into the problem during the approach to the equilibrium position is corrected by this direct solution for equilibrium mass transfer.

Even EQ6 executes considerably more slowly than a direct mass transfer program such as PHREEQE. Generally, the geochemical understanding of the system will be such that its definition using direct mass transfer computations will suffice. However, there will certainly be problems in which the identities and amounts of intermediate reaction products may be important and for these problems it may be simpler to use the reaction path code EQ6, because of the considerably less user input than is required to perform similar calculations with PHREEQE.

3 THERMODYNAMIC DATA REQUIREMENTS

EQ3/EQ6 and PHREEQE, like all other geochemical codes, are based on the principles of chemical thermodynamics. To simulate the aqueous speciation within a solution or to model a reaction path requires a value for the equilibrium constant for each mass action equation (2.1.2) at a temperature of interest as well as a value for the activity coefficients (eq. 2.1.3) for each dissolved species in the system.

A geochemical code cannot be used without a thermodynamic data base, so the authors of such codes customarily supply some thermodynamic data with their codes primarily so that new code users can run the codes as received and gain familiarity with their operation. These data bases are not intended for general application. As Parkhurst, Thorstenson and Plummer state in their description of PHREEQE (1980, pg. 42) "...the PHREEQE data base... is not documented in detail, and is intended only as a preliminary data base which may be used for testing purposes. The responsibility for final selection of thermodynamic data used by PHREEQE rests with the user".

It is presently the intention of the SCEPTER Program to supply with the geochemical codes PHREEQE and EQ3/EQ6 only preliminary thermodynamic data bases which will be useful for testing and model comparison purposes. The thermodynamic data bases required for specific applications of the codes will require compilation as part of those applications in the same way that hydraulic, thermal, and mechanical property data bases will be assembled for site specific applications.

The differences in the simulation modeling results which can be brought about by different choices of thermodynamic data are illustrated in several of the test problems in Chapter 4 in which comparisons are made between the results of running the same simulation using data originally supplied with PHREEQE against results obtained using data supplied with EQ3/EQ6.

The first section of this chapter discusses briefly the form in which equilibrium constant data are required by the two codes and mentions a number of recent thermodynamic data compilations which may

be of assistance to future users of these codes in assembling thermodynamic data bases for their specific applications.

The second section describes equations used by these codes to calculate activity coefficients and presents several comparisons of their results. The activity coefficient expressions included in the codes are intended for use in relatively dilute solutions and become less valid as the total solids content of the solutions increases. The illustrations in this section show the departure from reality of these expressions as the dissolved solids content of the solution increases. Thus, they form guides to potential code users as to the range of applicability of these codes.

3.1 EQUILIBRIUM CONSTANTS

Both EQ3/EQ6 and PHREEQE require temperature corrected values for the equilibrium constants of each reaction described by mass action equations (2.1.2) and for each dissolution/precipitation reaction (2.1.9). Both programs are structured so that the number actually required is the logarithm base 10 of the equilibrium constant (log K).

Log K values are functions of temperature and the codes include several expressions which describe this temperature dependence. EQ3/EQ6 expresses log K values using a polynomial expression:

$$\log K(t) = a + bt + ct^2 + dt^3 + et^4 \qquad (3.1.1)$$

where $\log K(t)$ = base 10 logarithm of the equilibrium constant K at temperature t;

t = temperature, in Celsius; and

a,b,c,d,e = polynomial coefficients.

The data set used with EQ3/EQ6 includes log K values at a number of temperatures-generally, 0, 25, 60, 100, 150, 200, 250, and 300 Celsius. Polynomials of the form of equation (3.1.1) are fit to these data and their coefficients a, b, c, d, e, rather than the data themselves, are input to EQ3/EQ6.

Two expressions for the temperature dependence of log K are used in PHREEQE. One is a polynomial expression of the form:

$$\log K(T) = a_1 + b_1 T + c_1/T + d_1 T^2 + e_1/T^2 \qquad (3.1.2)$$

with the temperature, T, in Kelvin (t + 273.15), and the other items as before.

PHREEQE also uses the van't Hoff equation, usually written:

$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \qquad (3.1.3)$$

or, in another form

$$\frac{d\,(R \ln K)}{d\,(1/T)} = -\Delta H^o \qquad (3.1.4)$$

in which: ln K = natural logarithm of the equilibrium constant;

R = gas constant = 8.3143 Joules/mol-Kelvin

T = Temperature, in Kelvin; and

ΔH^o = standard enthalpy of the reaction, (Joules/mol).

PHREEQE includes equation(3.1.4) written as

$$\log K(T) = \log K(T_r) - \frac{\Delta H^o}{R \ln 10}\left(\frac{1}{T} - \frac{1}{T_r}\right) \qquad (3.1.5)$$

which calculates the value of log K at temperature T from log K and ΔH^o values at a reference temperature T_r, of 25 C (298.15 K).

PHREEQE accepts thermochemical data for a given reaction either as log $K_{25\ C}$ and $\Delta H^o{}_{25\ C}$ values or as a set of values of the polynomial coefficients a_1, b_1, c_1, d_1 and e_1. The modified SCEPTER version of PHREEQE, can also use expression (3.1.1) and accepts values of the polynomial coefficients a, b, c, d, and e generated from the EQ3/EQ6 data bases.

The development of thermodynamic data bases suitable for performance assessment tasks will not be a trivial undertaking. It will be necessary, first, to identify the chemical elements which will be

important to the system being analysed. It is important that the data base include not only the elements whose radionuclides are important indicators of repository performance, but also those other elements present in major or in trace amounts which may control the water and rock chemical environment in which the radionuclides will be transported. Having identified the elements, it is necessary further to identify the aqueous species and ion complexes in which the elements may appear and to determine which solid and gaseous phases may be important in the system. Having identified the elements, solution, species, and solid and gaseous phases of importance in the system, and written reactions among them, it is necessary to have available log K values for each reaction over the range of temperatures which are likely to be encountered in the assessment calculation.

Robinson, Schafer and Haas (1981) have recently completed a study on the availability and feasibility of obtaining thermodynamic data on rock types of present interest to repository designers. While they conclude that sufficient reliable data do exist to evaluate the properties of most important mineral phases in these rock types, they also point out that significant effort is needed to compile them in an internally consistent form ready for use by geochemical modelers. They also do not address the availability of solution phase geochemical data.

A number of compilations of thermodynamic data are available and may be of assistance to a user in setting up a data base for a specific problem. Some of these sources will be listed briefly here to assist potential users.

In the WATEQ group of models (Table 1-1), each reaction considered is hard programmed into the code. Thus, data sets are an integral part of these codes and cannot be considered separately from them as they can when discussing the PHREEQE and EQ3/EQ6 codes. Data accompanying the WATEQ codes consist of log $K_{25\ C}$ and ΔH^{o}_{25} data for the reactions for use with equations like (3.1.5) or of polynomial coefficient values for use with expressions like (3.1.2). According to the authors of the WATEQ codes, the data are accepted only after evaluation of factors including the type of experiment from which they were derived and their consistency with

other data in the data set. Thus, the WATEQ data should form a reasonably consistent general data set and the WATEQ2 data have, in fact, been adopted by the authors of PHREEQE and comprise the preliminary data set supplied with that code.

The data supplied with the EQ3/EQ6 codes by Wolery also presumably represents an internally consistent set of data. As the results of the test problems described in Chapter 4 show, however, differences between the EQ3/EQ6 and WATEQ2/ PHREEQE data sets do exist and lead to considerable differences in simulation results when the different data sets are applied to certain problems. This is not to say that either the WATEQ2/PHREEQE data or the EQ3/EQ6 data is more correct than the other, only that they are different, and that these differences may lead to considerable differences in simulation results. These differences exemplify the need for careful data base compilation before applying either PHREEQE or EQ3/EQ6 to a real performance assessment problem.

There are several other compilations of critically evaluated data suitable for thermochemical modeling which should be mentioned. These include compilations of mineral and solution thermodynamic data by Robie, Hemingway and Fisher, (1978); and by Helgeson and others, (1978). These two are of interest because they include data not only at the reference temperature 25 C, but also at temperatures at least as high as a few hundred degrees C, as will be needed for geochemical modeling in the vicinity of the waste package itself. A more general compilation is the "Selected Values of Chemical Thermodynamic Properties" published by the U. S. National Bureau of Standards in their Technical Note 270 series. This compilation is limited, in that: First, only data at 25 C are reported so that they can be used only for simulations in the vicinity of that temperature where the van't Hoff expression (3.1.5) is valid; and, second, the sources of the data included are not given.

Recently a number of compilations of data of the sort useful for modeling nuclear waste chemical transport problems have been assembled. These include many values of reaction equilibrium constants, but they have not been critically evaluated either for their

experimental validity or for their consistency with other data on related reactions. Thus, information from them should be used with care. Reports by Ames and Rai, 1978; Benson and Teague, 1980; Rai and Serne, 1978 are in this category.

3.2 ACTIVITY COEFFICIENTS

Knowledge of the activity coefficients (γ_i) of each solution species and of the solvent is required by equations (2.1.3) to couple the set of mass balance equations (2.1.1), written in terms of species molalities, with the set of mass action equations (2.1.2), written in terms of species activities. The methods for calculating activity coefficients depend on whether the solvent or a charged or uncharged solute species is being considered. There is a limited choice of expressions in EQ3/EQ6, while PHREEQE users have several options for calculating activity coefficients of charged solute species.

3.2.1 Activity Of Liquid Water

The activity of the solvent, water, is a function of temperature and the total concentration of solutes. The EQ3/EQ6 expression for water activity is based on that given by Helgeson, and others, (1970):

$$\ln a_{H_2O} = -0.018 \sum \nu_{\underline{e}}\, m_{\underline{e}}\, \phi_{\underline{e}} \qquad (3.2.1)$$

in which: 0.018 Molecular Weight $H_2O/10^3$;

$\nu_{\underline{e}}$ = number of moles of ions in formula for electrolyte $\underline{e}$, (e.g., $\nu_{NaCl}=2$; $\nu_{CaCl_2}=3$);

$m_{\underline{e}}$ = molality of electrolyte $\underline{e}$; and

$\phi_{\underline{e}}$ = molal osmotic coefficient for electrolyte $\underline{e}$.

In EQ3/EQ6, the supporting electrolyte, $\underline{e}$, is taken to be NaCl, so that $\nu_{\underline{e}} = 2$ and $m_{\underline{e}} = I_{\underline{e}}$ is the stoichiometric ionic strength of an NaCl solution.

The expression for the osmotic coefficient, ϕ_e, includes four temperature dependent coefficients, values of which were derived from a fit to measured osmotic coefficient data of the type presented by Robinson and Stokes (1970, Appendices 8.3 and 8.8). Values of these constants at several temperatures are included in the data set supporting EQ3/EQ6.

The expression for water activity used by PHREEQE is that used in the WATEQ group of codes and adapted from one suggested by Garrels and Christ (1965, p. 64). Garrels and Christ point out that the change of water activity with temperature in the range of 0° to 100°C is not appreciable up to moderate dissolved electrolyte concentrations. Thus they write:

$$a_{H_2O} = 1 - 0.018\ \nu_e\ m_e \qquad (3.2.2)$$

Equation (3.2.1) and (3.2.2) become equivalent in the limit of dilute solutions.

When the measured activity of water is plotted against $\nu_e\ m_e$ for various electrolytes, the activity curves converge on a straight line with a slope of 0.017 in the range of $\nu_e m_e$ values of 4 to 3 and below, (cf. Garrels and Christ, 1965, fig. 2.16).

The empirical expression used in PHREEQE from Garrels and Christ is:

$$a_{H_2O} = 1 - 0.017\ \Sigma m_i \qquad (3.2.3)$$

where Σm_i is the sum of the molalities of dissolved anions, cations, and neutral species.

Table 3-1 compares measured a_{H_2O} values at 25 C with those calculated using equations 3.2.1 and 3.2.3. The measured and calculated values agree within 0.1% up to concentrations of 2 molal NaCl (I_e = 2). Those calculated using the EQ3/EQ6 expression also agree within 0.1% through 4.0 molal at all three temperatures, while the PHREEQE expression (3.2.3) predicts an a_{H_2O} nearly 3% higher than that measured at 6.0 molal at 25 C. Neither PHREEQE nor EQ3/EQ6 is intended for use in solutions more concentrated than a few molal. Thus, at least at temperatures below 100 C, there is little to recommend the use of the more complicated EQ3/EQ6 expression over the

Table 3-1: Activity of Water in NaCl Solutions as Measured and as Calculated Using the Expression in E03/E06 and PHREEQE.

m_{NaCl}	a_{H_2O} at 25°C measured 1/	a_{H_2O} at 25°C calculated using equation 3.2.3	a_{H_2O} at 25°C calculated using equation 3.2.1 2/	a_{H_2O} at 60°C calculated using equation 3.2.1 2/	a_{H_2O} at 100°C calculated using equation 3.2.1 2/
0.1	0.9966	.9966	.9966	.9967	.9967
0.2	0.9934	.9932	.9934	.9934	.9934
0.5	0.9836	.9830	.9835	.9836	.9836
1.0	0.9669	.9660	.9669	.9668	.9668
2.0	0.932	.932	.932	.931	.931
3.0	0.893	.898	.893	.893	.893
4.0	0.852	.864	.852	.852	.852
5.0	0.807	.830	.807	.809	.811
6.0	0.760	.796	.760	.765	.770

1/ Measured values, from Robinson and Stokes, 1970, Appendix 8.3

2/ Using osmotic coefficients calculated as in E03/6

000039

6790

simpler equation used in PHREEQE.

3.2.2 Neutral Solute Species

Expressions for the activity coefficients of neutral (uncharged) species rest mainly on measured activity coefficients of CO_2 dissolved in electrolyte solutions of various temperatures. To calculate γCO_2, EQ3/EQ6 uses the expression:

$$\log \gamma CO_2 = c_1 I + c_2 I^2 + c_3 I^3 + c_4 I^4 \qquad (3.2.4)$$

where I is the ionic strength and c_1 through c_4 are temperature dependent constants derived from fitting equation 3.2.4 to experimental data (Cf. Helgeson, 1969). These constants are included in the data set supporting EQ3/EQ6.

Few other data exist from which activity coefficients as precise as those known for CO_2 can be found. The available data do suggest that activity coefficients of different neutral species in a given salt solution are similar (Helgeson, 1969), and so activity coefficients for other neutral species are frequently taken as equal to that of CO_2 in the same solution. This option is available in EQ3/EQ6.

A much simpler empirical equation than 3.2.4 was suggested by Garrels and Christ (1965, p. 69) and Helgeson (1969):

$$\log \gamma = c_0 I \qquad (3.2.5)$$

where c_0 is a function of temperature. This equation is also available in EQ3/EQ6 with c_0 taken as equal to the Debye-Huckel BDOT value at the solution temperature.

The activity coefficients of all neutral species except the dissolved gases in EQ3/EQ6 are taken as 1 by setting C_0 in equation 3.2.5 to zero, in accordance with the suggestion of Helgeson and others (1970, p.574) for moderately polar, neutral species.

PHREEQE uses a single activity coefficient expression for all neutral species, which is simply 3.2.5 with $C_0 = 0.1$. This expression is also used in the predecessor programs to PHREEQE, WATEQ (Truesdell and Jones, 1974), and WATEQF (Plummer, Jones and Truesdell, 1976), but no source for it is referred to in the descriptions of any of the three codes.

Table 3-2 compares the values of activity coefficients calculated using these expressions. Values from the simple PHREEQE expression are within a few percent of the measured values for γCO_2 as smoothed by equation 3.2.4 to an ionic strength of about 5 molar. Values from equation 3.2.5 with C_o = BDOT show poorer agreement, however. At temperatures of 60 and 100 C, agreement between values from equations 3.2.5 and 3.2.6 with C_o = BDOT is still poor, and it appears that 3.2.5 with C_o = 0.1, in spite of its independence of temperature, is still adequate though to lower ionic strengths.

3.2.3 Charged Solute Species

Activity coefficients of ionic (charged) solutes are calculated using the extended Debye-Huckel expression, or some variant of it. This expression as it appears in both EQ3/EQ6 and PHREEQE is written:

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I \qquad (3.2.6)$$

where: A, B = Debye-Huckel constants, functions of temperature and dielectric constant of the solvent (Robinson and Stokes, 1970, p. 230; Truesdell and Jones, 1974, p. 241)

z_i = charge on ion i

I = Ionic strength of solution

$= 1/2 \ \Sigma m_i z_i^2$

Values of A and B at various temperatures are given in the data supporting EQ3/EQ6. In PHREEQE, the full equations for A and B (Truesdell and Jones, 1974) appear and A and B are calculated from them.

The extended Debye-Huckel as originally proposed included only the first term on the right in equation 3.2.6, with a_i equal to a_i^o, an ion size parameter. Values of a_i^o calculated by Kielland, (1937) are accepted in the data sets of both EQ3/EQ6 and PHREEQE.

While the extended Debye-Huckel equation adequately accounts for decreasing activity coefficients with increasing ionic strengths at low ionic strengths (<0.1), it does not reproduce the increase of activity coefficients at higher ionic strengths. This reversal has led to the inclusion of the second term on the right equation 3.2.6.

Table 3-2: Activity Coefficients of Neutral Species in NaCl Solutions Calculated Using Expression in EQ3/EQ6 and PHREEQE.

I	ACTIVITY COEFFICIENTS OF NEUTRAL SPECIES at 25 C from Equation 3.2.4 1/	Equation 3.2.5 2/	Equation 3.2.5 3/	at 60 C from Equation 3.2.4 1/	Equation 3.2.5 2/	at 100 C from Equation 3.2.4 1/	Equation 3.2.5 2/
0.1	1.026	1.009	1.023	1.022	1.010	1.0186	1.0106
0.2	1.052	1.019	1.047	1.044	1.020	1.037	1.0214
0.5	1.132	1.048	1.122	1.111	1.052	1.0959	1.0544
1.0	1.270	1.099	1.259	1.230	1.010	1.200	1.1117
2.0	1.570	1.208	1.585	1.490	1.225	1.4400	1.2359
3.0	1.929	1.327	1.995	1.780	1.355	1.7397	1.3740
4.0	2.409	2.459	2.512	2.100	1.500	2.1314	1.5276
5.0	3.122	1.603	3.162	2.450	1.660	2.6667	1.6982
6.0	4.285	1.762	3.981	2.828	1.837	3.4271	1.8880

1/ Coefficients C_1 through C_4 from EQ3/EQ6 data

2/ C_o = BDOT calculated from data in EQ3/EQ6

3/ C_o = 0.1, as in PHREEQE

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In EQ3/EQ6, b_i is the same for all ions, and is equal to the deviation function B (BDOT) described by Helgeson, (1970, p.748), following Lewis and Randall, (1961). BDOT is taken as independent of ionic strength, I, or electrolyte type but is temperature dependent. Its value at several temperatures appears in the supporting data file for EQ3/EQ6.

Several expressions for calculating ionic activity coefficients are included in PHREEQE. The one used for any given ion is selected by the user. The PHREEQE expressions include:

i) The extended Debye-Huckel expression;

ii) The Davies equation, which appears in PHREEQE as:

$$\text{Log } \gamma_i = - A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - dI \right) \qquad (3.2.7)$$

where the constants are as above. This equation is referred to by Robinson and Stokes (1970, p.232) where d = 0.1. Stumm and Morgan (1981, tab 3.3) give d = 0.3, and the latter value is used in PHREEQE.

iii) An expression called the WATEQ Debye-Huckel equation can also be used. This equation is identical with 3.2.6, but the values of a_i and b_i are not the same as when the equation is used in EQ3/EQ6. These coefficients in the WATEQ Debye-Huckel result from fitting the equation to activity coefficients from mean salt data, as described by Truesdell and Jones (1974). These coefficients are given in the PHREEQE data set only for the ions:

Ca^{+2}, Mg^{+2}, Na^+, K^+, HCO_3^-, CO_3^{-2}, SO_4^{-2}, and Cl^-

The SCEPTER version of PHREEQE contains all the activity coefficient options of the original code, but has been modified so it can also use the EQ3/EQ6 form of the Debye-Huckel expression with b_i = BDOT.

Activity coefficient values calculated using these various expressions are shown in Figures 3-1 and 3-2. Comparisons for a univalent cation (Na^+) and anion (Cl^-) and a divalent cation (Ca^{+2}) and anion (SO_4^{-2}) are given at 25 and 60 C.

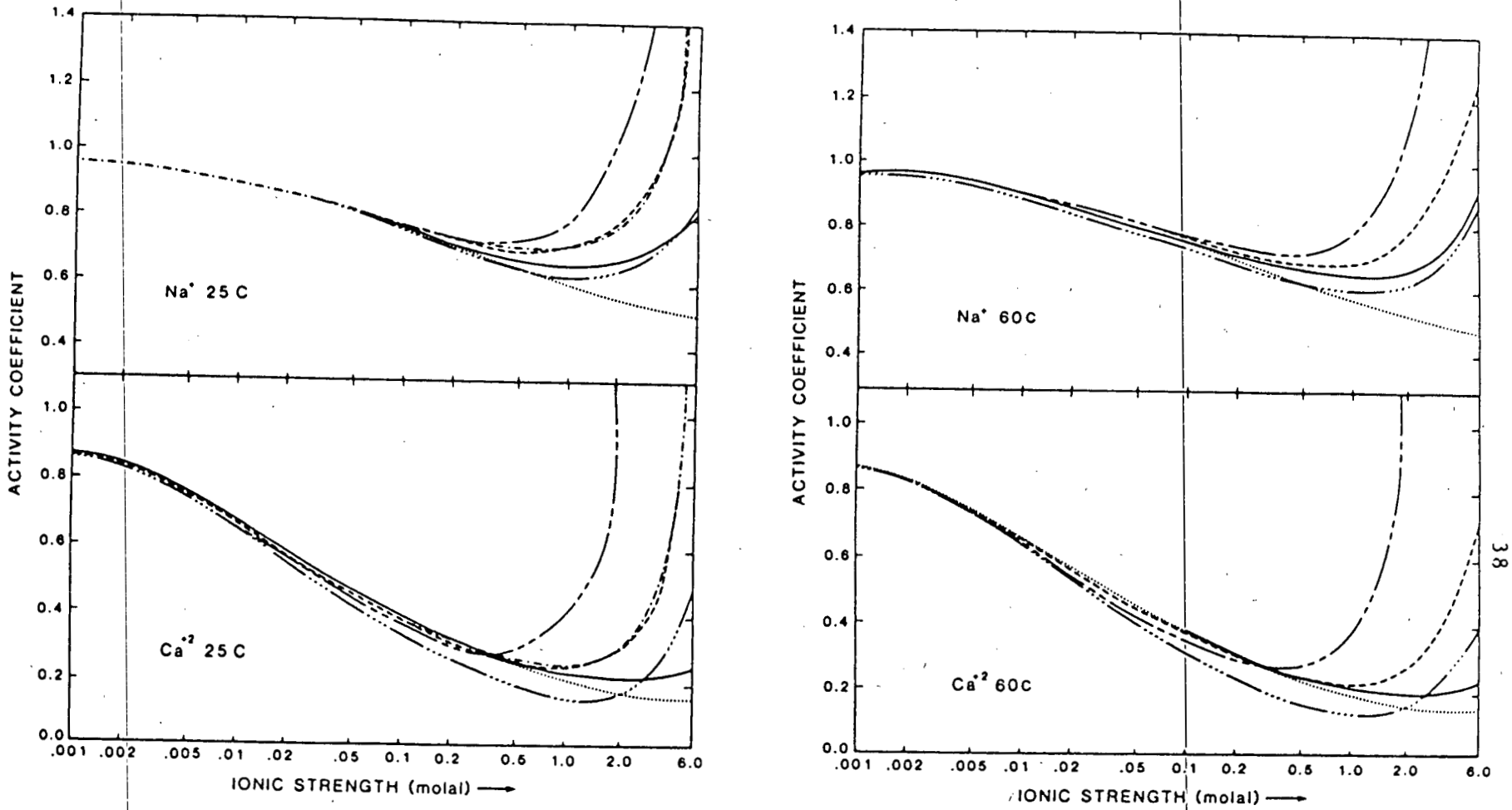
Experimental activity coefficients derived from mean salt data (Truesdell and Jones, 1974, Tab. 3) are also given. For perspective when using these plots it is useful to keep in mind that the ionic strength of sea water is about 0.7 molal, while that of a saturated halite (NaCl) solution is about 6.2 mol at 25 C and 6.3 mol at 60 C (Gevantman, 1981).

Figures 3-1 and 3-2 show that the experimental mean-salt data are best reproduced by the WATEQ Debye-Huckel expression. This is not surprising because the parameters a_i and b_i were evaluated simply by fitting equation 3.2.6 to these same mean-salt data (Truesdell and Jones, 1974). In spite of its ability to reproduce experimental activity coefficient data, the WATEQ Debye-Huckel approach will have only limited utility in performance assessment applications because of the general lack of activity coefficient data for the unusual elements which must be considered in these applications. The WATEQ Debye-Huckel approach will be useful though in making the sorts of relatively simple calculations which will be required to investigate halite solution effects around salt deposits where only major elements need be considered for which WATEQ Debye-Huckel coefficient values are available.

At ionic strengths below 0.1 molar the results of the various expressions group nicely except for the Davies expression with d=0.1 which predicts lower activity coefficients for the divalent cation Ca^{+2} (figure 3-2). At higher ionic strengths the conventional Debye-Huckel expression does not reproduce the inflection at ionic strengths of about 1 molar because it contains no term directly dependent on ionic strength. The Davies equation and the Debye-Huckel with b_i equal to BDOT follow this inflection with varying degrees of success. The Davies equations with d=0.3 predicts activity coefficients higher than those predicted by any other equations for all ions at ionic strengths of 0.5 and above.

As all the figures show, there is likely to be considerable uncertainty in the activity coefficient values calculated using any of the expressions available in PHREEQE or EQ3/EQ6 for waters with ionic

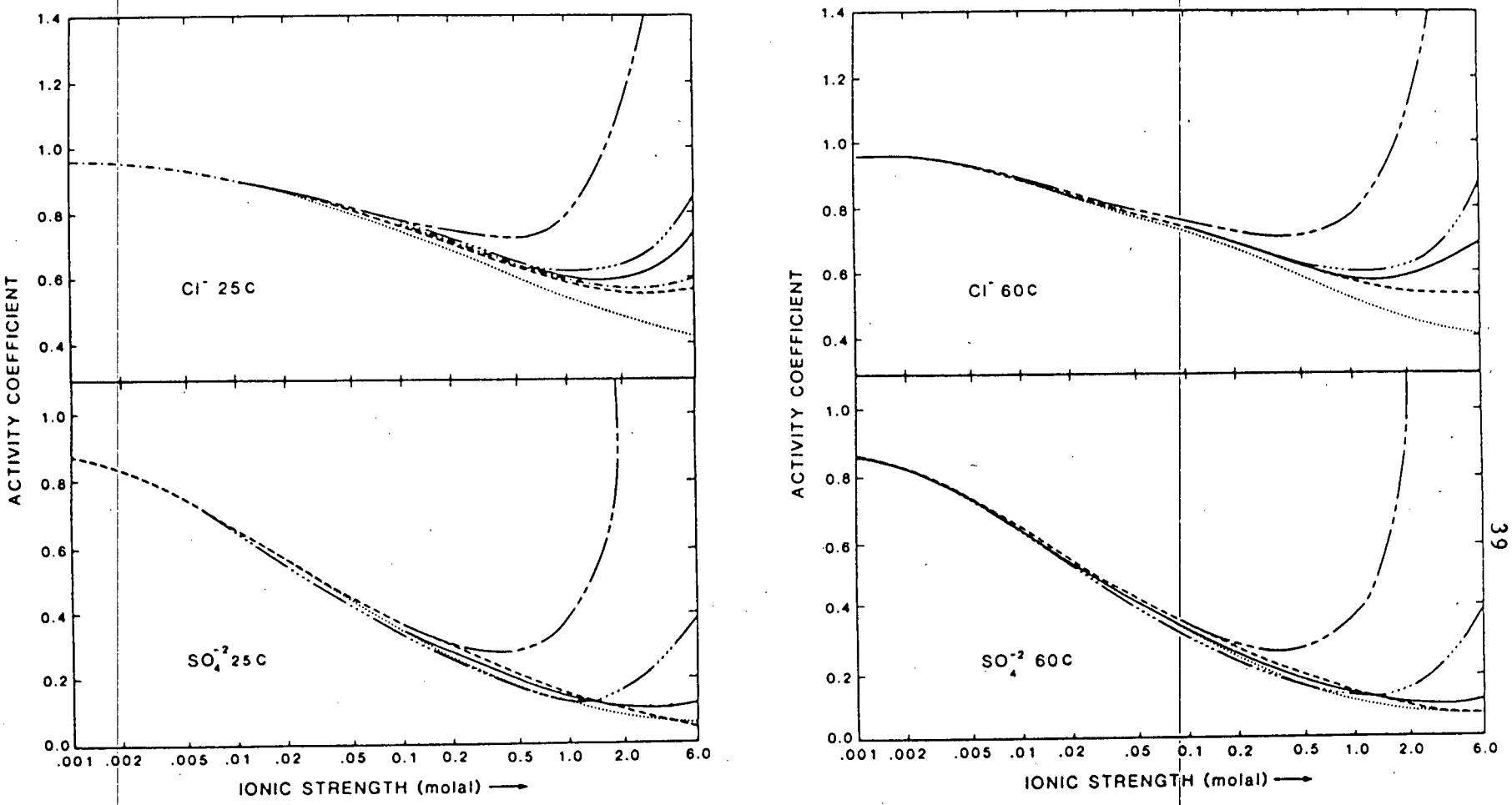
strengths in excess of about 1 molar. For this reason neither code is particularly appropriate for use in waters of high ionic strengths, although for such simple calculations as salt dissolution, PHREEQE used with the WATEQ Debye-Huckel expression should be adequate.



Debye - Hückel expressions : (3.2.6)
- Extended : $b_i = 0$
- EQ3/6 : b_i = BDOT
- WATEQ : a_i, b_i fit to mean salt data.

Davies equation (3.2.7)
- d = 0.1
- d = 0.3
- Mean salt data (Truesdell and Jones, 1974)

Figure 3-1: Activity Coefficients of Na^+ and Ca^{+2}.



Debye - Hückel expressions : (3.2.6)
- Extended : $b_i = 0$
- EQ3/6 : b_i = BDOT
- WATEQ : a_i, b_i fit to mean salt data.

Davies equation (3.2.7)
- d = 0.1
- d = 0.3
- Mean salt data (Truesdell and Jones, 1964)

Figure 3-2: Activity Coefficients of Cl^- and SO_4^{-2}.

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4 CODE COMPARISON AND VERIFICATION PROBLEMS

Five test problems were run using both the PHREEQE and EQ3/EQ6 codes. The problems were designed to:

- o Provide code verification by means of code-to-code and code-to-hand calculation comparison; and
- o To illustrate and test the various operating options available in the codes.

Verification by code-to-code comparison is demonstrated by the achievement of essentially identical results when two codes are applied to the same problem. It is necessary therefore that not only the geochemical problem description supplied to each to be the same, but that the thermodynamic data base used also be the same. Two thermodynamic data sets were available. One was the preliminary PHREEOE data set included in the published code description (Parkhurst, Thorstenson and Plummer, 1980) and referred to here as the PREPHR set. The second was the data file set DEQPAK7 which accompanied version 3015J of EQ3 and EQ6. The PREPHR data set is structured so as to be read directly by PHREEQE. The DEQPAK7 data though, requires manipulation by a code EQTL, which is supplied as part of the EQ3/EQ6 software package, before it can be used by those codes.

To test each code with both data bases required the modification and development of data handling codes. An extensively modified version of EQTL is used to write DEQPAK7 data in a form readable by PHREEQE. This modified EQTL which is called PHTL is described with the SCEPTER PHREEQE documentation (INTERA, 1982a). Certain minor modifications to PHREEQE were also required so that it could use PHTL output. These modifications are also described by INTERA, 1982a.

It was also important that the PREPHR data be available for use by EQ3/EQ6 and so code PQTL was assembled to make this possible. This code is described as part of the EQ3/EQ6 documentation (INTERA, 1982b).

The fact that most of the problems were run using two data sets also makes them of interest as illustrating the disparities in results which may come about from differences in the thermodynamic data sets used with geochemical models.

4.1 TEST PROBLEM 1: SPECIATE MAJOR IONS OF SEA WATER

The ion-association model was first applied to geochemistry by Garrels and Thompson (1962) who used it to describe the major ion chemistry of sea water. Summarizing their work here serves to:

- Illustrate the use of the aqueous speciation model described in Section 2.1; and
- To verify the coding of the computational algorithms in both PHREEQE and EQ3/EQ6 by comparing their output with the results hand-calculated here.

4.1.1 Input

The major ion composition of sea water is dominated by seven elements. Their concentrations, in molality (moles per kg H_2O) as given by Nordstrom and others (1979, tab III) are:

Sodium	(Na^+)	0.4854	Chlorine	(Cl^-)	0.5658
Potassium	(K^+)	0.0106	Sulfur	(SO_4^{-2})	0.0293
Calcium	(Ca^{+2})	0.0107	Carbon	(HCO_3^-)	0.00186
Magnesium	(Mg^{+2})	0.0551		(CO_3^{-2})	0.00022

Sulfur and carbon can occur in several oxidation states in the range of conditions which occur naturally at or near the earth's surface. They are present in sea water in their oxidized states, with sulfur represented by sulfate (SO_4^{-2}), and carbon commonly present as bicarbonate (HCO_3^-) and carbonate (CO_3^{-2}). Concentrations of the latter ions are reported separately so individual analyzed values for them are given in the table.

A total of 20 ion pair complexes are theoretically possible from combinations of the four cations and four anions in the table, plus the hydroxide anion (OH^-) which commonly forms ion pairs. However, some of these 20 are either unknown or are so weakly associated that they can be neglected. Chloride (Cl^-) and hydroxide (OH^-)

complexes were considered by Garrels and Thompson (1962) to be so weak at 25 C that they were not included in their treatment of sea water.

Log K values for these ion pair reactions are given in Table 4-1. Values contained in the PREPHR and DEQPAK7 data sets are included. The PREPHR values were used in the hand calculations.

The meaning of these constants can be illustrated using the $CaSO_4^o$ ion pair. This pair associates according to the reaction:

$$Ca^{+2} + SO_4^{-2} = CaSO_4^o$$

for which the mass action equation (2.1.2) can be written:

$$a_{CaSO_4^o} = K_{CaSO_4^o} * a_{Ca^{+2}} * a_{SO_4^{-2}} \qquad (4.1.1)$$

From Table 4-1 $\log K_{CaSO_4^o} = 2.31$

Given the analyzed species concentrations and the identities of the solution complexes to be considered, the mass balance equations (2.1.1) can now be written. There are nine such equations, one for each of the eight analyzed species and one for OH^-. For Ca^{+2}, for example; one writes:

$$m_{T,Ca^{+2}} = m_{Ca^{+2}} + m_{CaHCO_3^+} + m_{CaCO_3^o} + m_{CaSO_4^o} + m_{CaOH^+} \qquad (4.1.2)$$

For each ion pair concentration term in the mass balance equations, one mass action equation exists. Equation 4.1.1 corresponds to the $m_{CaSO_4^o}$ term in 4.1.2, for example. To combine them requires values for the activity coefficients of the free and complexed ions (Equation 2.1.3). The evaluation of activity coefficients was discussed at length in Section 3.2, but for the purposes of this test problem it is expedient to adopt the set of published values for sea water activity coefficients given in Table 4-2. The ionic strength of sea water is about 0.7. The values in this table are well within the range of values calculated by the several procedures available within PHREEQE and EQ3/6 and given in Figures 3-1 and 3-2 for water of an equivalent ionic strength.

Table 4-1: Log Association Constants of Ion Pairs at 25 C in Simple Sea Water Test Problem. Values Contained in the PREPHR and DEQPAK7 Data Bases are Given. PREPHR Values were Used in Hand Calculations.

CATION	DATA SET	ANION HCO_3^-	CO_3^{-2}	SO_4^{-2}	Cl^-	OH^-
Na^+	PREPHR	-0.25	1.27	0.70	-----	-----
	DEQPAK7	-----	0.96	0.72	-0.91	-0.68
K^+	PREPHR	-----	-----	0.85	-----	-----
	DEQPAK7	-----	-----	0.85	-----	-----
Ca^{+2}	PREPHR	1.02	3.15	2.31	-----	1.40
	DEQPAK7	1.25	3.20	2.31	-----	1.40
Mg^{+2}	PREPHR	1.07	2.98	2.25	-----	2.20
	DEQPAK7	1.08	2.98	2.25	-----	2.21

4.1.2 Results:

Hand Calculations: To make hand-calculations of sea-water speciation tractable, Garrels and Thompson (1962) assumed that because chloride is the dominant anion in sea water, yet is not part of any complexes being considered here, a reasonable first step in solving the mass balance and mass action equations would be to neglect the effect of complexing on cation concentrations and assume that, for example, $m_{Ca^{+2}} = m_{T,Ca^{+2}}$. The free anion concentrations can now be found directly as follows, using CO_3^{-2} as an example.

CO_3^{-2} mass balance:

$$m_{T,CO_3^{-2}} = m_{CO_3^{-2}} + m_{NaCO_3^-} + m_{CaCO_3^o} + m_{MgCO_3^o}$$

$NaCO_3^-$ mass action:

$$a_{NaCO_3^-} = K_{NaCO_3^-} * a_{Na^+} * a_{CO_3^{-2}}$$

$$m_{NaCO_3^-} = (K_{NaCO_3^-} * m_{Na^+} * {}_{Na^+} * m_{CO_3^{-2}} * {}_{CO_3^{-2}}) / \gamma_{NaCO_3^-}$$

Substituting K and γ values from tables 4-1 and 4-2 and assuming $m_{Na^+} = m_{T,Na^+}$:

$$m_{NaCO_3^-} = 1.8077 * m_{CO_3^{-2}}$$

Table 4-2: Activity Coefficients of Major Free Ions and Ion Pairs in Sea Water. Data from Holland (1978, Table 5-4).

	Free Ions	HCO_3^-	CO_3^{-2}	SO_4^{-2}	Cl^-
		.68	.20	.18	0.62
Na^+	.68	1.13	.68	.68	1.13
K^+	.62	--	--	.68	--
Ca^{+2}	.22	.68	1.13	1.13	--
Mg^{+2}	.25	.68	1.13	1.13	--

$CaCO_3^o$ mass action: (similar to $NaCO_3^-$)

$$m_{CaCO_3^o} = 0.5885 * m_{CO_3^{-2}}$$

$MgCO_3^o$ mass action: ~~(similar to $NaCO_3^-$)~~

$$m_{MgCO_3^o} = 2.3283 * m_{CO_3^{-2}}$$

Substituting in CO_3^{-2} mass balance:

$$m_{T,CO_3^{-2}} = m_{CO_3^{-2}} (1 + 1.8077 + 0.5885 + 2.3283)$$

$$m_{CO_3^{-2}} = 0.00022/5.7245 = 3.84E-05$$

$$= 17\% \text{ of } m_{T,CO_3^{-2}}$$

Substituting in mass action equations:

$$m_{NaCO_3^-} = 3.84E-05 * 1.8077 = 6.94E-05 \ (32\%)$$

$$m_{CaCO_3^o} = 3.84E-05 * 0.5885 = 2.26E-05 \ (10\%)$$

$$m_{MgCO_3^o} = 3.84E-05 * 2.3283 = 8.95E-05 \ (41\%)$$

The percentages are those of the ion pairs with respect to the total CO_3^{-2} concentration.

Similar calculations for HCO_3^- and SO_4^{-2} lead to:

$m_{HCO_3^-}$	= 1.43E-03 (77%)	$m_{SO_4^{-2}}$	+ 1.53E-02 (52%)
$m_{NaHCO_3^o}$	= 1.60E-04 (9%)	$m_{NaSO_4^-}$	= 6.69E-03 (23%)
$m_{CaHCO_3^+}$	= 3.52E-05 (2%)	$m_{KSO_4^-}$	+ 1.88E-04 (1%)
$m_{MgHCO_3^+}$	= 2.32E-04 (12%)	$m_{CaSO_4^o}$	= 1.17E-03 (4%)
		$m_{MgSO_4^o}$	= 5.96E-03 (20%)

Concentrations for all complexes are now available and it remains to calculate the free cation concentrations from the cation mass balance equations. For example:

$$m_{Na^+} = m_{T,Na^+} - m_{NaHCO_3^o} - m_{NaCO_3^-} - m_{NaSO_4^-}$$

$$= 4.854E-01 - 1.60E-04 - 6.94E-05 - 6.69E-03$$

$$= 0.4785 \ (= 99\% \ m_{T,Na^+})$$

Similarly:

$$m_{K^+} = 0.0104 \ (98\%)$$

$$m_{Ca^{+2}} = 0.0095 \ (88\%)$$

$$m_{Mg^{+2}} = 0.0488 \ (89\%)$$

The assumption made in this set of calculations - that the cations are not significantly complexed - is borne out for Na^+ and K^+, but is less adequate for Ca^{+2} and Mg^{+2}. The calculation can be refined by iterating through it once more, this time using the free cation concentrations just calculated in place of the total cation concentrations used in the first iteration. The results of such a second iteration are shown in Table 4-3.

Table 4-3: Percents of Total Concentrations for Free Ions and Important Ion Pairs in Simple Sea Water, as Calculated by Hand and by PHREEQE and EQ3.

		Free Ion	HCO_3^- Pair	CO_3^{-2} Pair	SO_4^{-2} Pair
Na^+	1)	98.6	0.0	0.0	1.4
	2)	98.6	0.0	0.0	1.3
	3)	96.0	---	0.0	1.2(+2.7% NaCl)
K^+	1)	98.1	---	---	1.8
	2)	98.4	---	---	1.6
	3)	98.3	---	---	1.7
Ca^{+2}	1)	88.8	0.3	0.2	10.6
	2)	88.6	0.3	0.2	10.8
	3)	88.0	0.6	0.3	11.2
Mg^{+2}	1)	88.6	0.4	0.2	10.7
	2)	88.5	0.4	0.2	10.9
	3)	87.0	0.5	0.2	12.3

		Free Ion	Na^+ Pair	K^+ Pair	Ca^{+2} Pair	Mg^{+2} Pair
HCO_3^-	1)	78.5	8.6	---	1.6	11.3
	2)	78.2	8.6	---	1.7	11.5
	3)	81.3	--	---	3.2	15.4
CO_3^{-2}	1)	18.6	33.2	---	9.5	38.6
	2)	17.5	30.3	---	10.4	41.7
	3)	19.1	15.1	---	13.3	52.4
SO_4^{-2}	1)	53.8	23.2	0.6	3.6	18.6
	2)	53.1	21.8	0.6	4.0	20.5
	3)	51.9	21.0	0.6	4.1	23.3

1) Hand calculated, as above, with PREPHR data

2) PHREEQE results, with PREPHR data base.

3) EQ3 results, with DEQPAK7 data base.

The free ion concentrations differ by only a percent or less from those calculated by the first iteration. This suggests that little additional precision would result from a third iteration made using the cation concentrations from the second iteration, so the hand calculations stopped here.

PHREEQE and EQ3 Calculations: The solution composition data used for the hand-calculations were also used as input to the two codes. The equilibrium constant values used were those for the data sets supplied with the codes. That is, PREPHR data were used in the PHREEQE calculations and DEQPAK7 for the EQ3 calculations (Table 4-1).

Because these calculations are intended to distribute total measured ion concentrations among free ions and ion pairs, it is appropriate to express the results of these code runs as percentages of the total ion concentrations represented by ion pairs and free ions. These results together with those from the hand-calculations are given in Table 4-3.

4.1.3 Discussion

The results of the three sets of calculations are shown in Table 4-3. While the agreement among them is generally good, there are some points of difference which require further discussion.

The PHREEQE and hand calculations were made using the same set of equilibrium constant values, and so the two sets of results should agree closely, as they do. The EQ3 results using the DEQPAK7 data show some differences from the other two sets. The results for Na^+, for example, are different because of the inclusion in the DEQPAK7 data set of an NaCl ion pair and the absence of an $NaHCO_3^o$ pair. Similarly, the PHREEQE and hand-calculated results for the HCO_3^- ion and its pairs agree well while the EQ3 results suggest larger percentages both of free HCO_3^- ions and of calcium and magnesium pairs because of the absence in the DEQPAK7 data set of the rather strong $NaHCO_3^o$ pair.

On an overall basis though, the results compare closely enough to show that the algorithms are coded correctly by virtue of their ability to reproduce the hand-calculated results.

4.2 TEST PROBLEM 2: SPECIATE FULL SEA-WATER ANALYSIS

Sea water contains measurable quantities of most of the elements in the periodic chart, and has been carefully analyzed many times. Such a complex, well-known solution is ideal for demonstrating and testing the capabilities of aqueous speciation models, and it has been used for that purpose by many authors. Including a sea-water problem here is useful to compare the ability of the two codes to handle complex solutions, to compare the output of each with the published results of other code comparison studies, and to illustrate the extent of the data bases accompanying the present versions of the codes.

4.2.1 Input

Input required includes both solution analytical data and thermodynamic data. Both the PREPHR and DEQPAK7 data sets described in Chapter 3 were used.

The analytical data used are given in Tables 4-4 and 4-5. To facilitate comparison with the code comparison results of Nordstrom and others (1979), the concentrations given in their Table III were adopted. Because the concentrations of certain minor elements represented in the DEQPAK7 data base were not given by Nordstrom and others, minor element concentrations reported by Holland (1978, Table 5-2) are also given in Table 4-5, and were used where needed in the code comparisons.

Tables 4-4 and 4-5 also indicate the data sets in which the constituent is included. In addition to the PREPHR data supplied with PHREEQE and DEQPAK7 with EQ3/EQ6, a comprehensive thermodynamic data set has recently been published by Ball, Nordstrom and Jenne (1980) for use with WATEQ2 (see Table 1-1). The inclusion of a constituent in the WATEQ2 data set is also shown in Tables 4-4 and 4-5.

Each code has a number of input options. Complete description of these options are given in the descriptions of the codes themselves and will not be repeated here. For documentation of these results, however, the options chosen here are listed.

Table 4-4: Major Dissolved Ion Content of Sea Water and Values of Other Parameters. From Nordstrom and Others (1979, Table III).

CONSTITUENT		Concentration in milligram/kg soln. (ppm)	Included In DEOPAK7 (D), PREPHR (P) and WATEO2 (W) Data Sets
Sodium	Na^{+}	10768.	D,P,W
Magnesium	Mg^{+2}	1291.8	D,P,W
Calcium	Ca^{+2}	412.3	D,P,W
Potassium	K^{+}	399.1	D,P,W
Strontium	Sr^{+2}	8.14	D,P,W
SUM CATIONS (meq/kg)		605.648	
Chloride	Cl^{-}	19353.	D,P,W
Sulfate	SO_4^{-2}	2712.	D,P,W
Alkalinity 1/ as	HCO_3^{-}	141.682	D,P,W
Bromide	Br^{-}	67.3	P,W
Fluoride	F^{-}	1.39	D,P,W
SUM ANIONS (meq/kg)		605.581	
Silica	SiO_2	4.28	D,P,W
Boron	B	4.45	P,W
SUM DISSOLVED SOLIDS (ppm)		$35. \times 10^3$	D
OTHER PARAMETERS:			
pH		8.22	D,P,W
pE (0.500 volts)		8.45	D,P,W
Density (gm/cc)		1.02336	D,P,W
Temperature (C)		25.	D,P,W

1/ Total carbonate as HCO_3 = 123.377 ppm. (See Table 4.2.3)

Table 4-5: Minor Constituents of Sea Water. From Nordstrom and Others (1979, Table III) and from Holland (1978, Table 5-2).

ELEMENT	FORM	Concentration in Micrograms/kg soln. (ppb) Nordstrom	Holland	Included In DEQPAK7 (D), PREPHR (P) and WATEQ2 (W) Data set
Silver	Ag	0.04	0.008	D,W
Aluminum	Al	2.	2.	D,P,W
Arsenic	$As(OH)_4^-$	8.	6.	D,W
Gold	Au	--	0.005	D
Barium	Ba	20.	20.	D,P,W
Cadmium	Cd	0.1	0.1	W
Cesium	Cs	0.4	0.4	D,W
Copper	Cu	0.7	0.3	D,W
Iron	Fe	2.	2.	D,P,W
Mercury	Hg	0.03	0.02	D
Iodine	I	62.	60.	W
Lithium	Li	181.	180.	P,W
Manganese	Mn	0.2	0.2	D,P,W
Nitrogen				
Nitrate	NO_3^-	290.		D,P,W
Nitrite	NO_2^-	20.		W
Ammonium	NH_4^+	30.		D,W
Nickel	Ni	1.7	0.6	W
Phosphorus	PO_4^{-3}	60.	60.	D,P,W
Lead	Pb	0.05	0.03	D,W
Rubidium	Rb	117.	120.	W
Uranium	U	--	3.3	D
Vanadium	VO^{+2}	--	3.3	D
Zinc	Zn	4.9	3.	D,W
Zirconium	ZrO^{+2}	--	0.04	D

Input concentrations: Molality (m), the number of moles of a solute per kilogram of water is the concentration unit used by both EQ3/EQ6 and PHREEQE in their calculations. Water analytical data of the sort likely to be input to either program only rarely are given as molalities and so for convenience, both codes include routines for converting concentrations entered in any of several units to molality.

Analyzed solute concentrations are usually expressed as masses of solute per mass or volume of solution, in, for example:

$$mg/\ell = \frac{\text{milligrams solute}}{\text{liter solution}} \text{ ; or}$$

$$ppm = \frac{mg}{kg} = \frac{\text{milligram solute}}{\text{kilogram solution}} .$$

It is also not uncommon to find solution composition given as:

$$\text{Molarity} = \frac{\text{Moles solute}}{\text{liters solution}}$$

Conversion of the units entered to molality requires values for the solution density (ρ) and for its total dissolved solids content (TDS). Both codes require the entry of a density value (or assign it a default value of 1). EQ3 also requires that TDS, in mg/ℓ or ppm, be entered, while PHREEQE calculates TDS from the solution composition entered.

The units conversion is a straightforward combination of the expressions:

$$mols_i = mg_i * \frac{10^3}{GFW}$$

$$kg_{soln} = \ell_{sol} * \rho$$

$$\frac{kg_{soln}}{kg_{H_2O}} = 1/(1 - \frac{TDS(ppm)}{10^6})$$

with the definitions of particular units as given above.

Inputs for this problem were in milligrams per kilogram solution (ppm) as given in tables 4-4 and 4-5. The solution density input and the total dissolved solids required by EQ3 are also in table 4-4.

Oxidation potential: EQ3 accepts a number of measures of oxidation potential, including oxygen fugacity, Eh (volts), pe, or as determined by a specified redox reaction couple. pe is defined:

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

$$= \left[\frac{\text{Faraday}}{\ln 10 * \text{Gas Constant} * \text{Abs. Temp}}\right] * \text{Eh (volts)}$$

$$= 16.90 * \text{Eh (volts)} \text{ @ } 25\text{ C.}$$

PHREEQE accepts only pe, so for comparability, the pe given in Table 4-4 was input to both codes.

Alkalinity and carbonate species: Alkalinity is the capacity of an aqueous solution to neutralize strong acids. The dissolved carbonate species CO_3^{-2} and HCO_3^- are the dominant contributors to the alkalinity of most waters by their participation in the reactions:

$$CO_3^{-2} + H^+ = HCO_3^-$$

$$HCO_3^- + H^+ = CO_{2,aq} + H_2O$$

Adding H^+ to a solution drives these reactions to the right until at a pH of about 4.5, they are essentially complete. The number of equivalents of H^+ required equals equivalents of HCO_3^- plus CO_3^{2} and is the carbonate alkalinity of the system. Carbonate alkalinity is an optional input to EQ3.

Alkalinity can also include contributions from other species with a capacity to neutralize H^+ ion. Such species as $Al(OH)_4^-$ react with H^+ to form Al^{+3} or $Al(OH)_2^+$, for example, while $H_3SiO_4^-$ reacts to H_4SiO_4, and both add to the titration alkalinity. Both PHREEQE and EQ3 accept titration alkalinity as input, and correct it for the presence of non-carbonate, H^+ reactive species to reach a carbonate value.

Some analyses report total dissolved carbonate ($CO_{2,aq}$ + HCO_3 + CO_3^{-2}) instead of alkalinity, and PHREEQE and EQ3 can accept this input as well.

To compare the ability of the two codes to handle the several carbonate input options, each was run with both titration alkalinity and total carbonate options.

Electrical Neutrality: Both codes have two options to adjust the calculated solution to electrical neutrality, as well as a third option, to ignore electro-neutrality. Electrical balance can be achieved by adding a specified anion (generally Cl^-) or cation (Na^+ or K^+) or by changing the pH. For this test problem, electrical balance was ignored.

Activity coefficients: The activity coefficent options are described at length in Section 3.2. Several were used for this problem for more adequate code result comparisons and for comparison with the published results of other codes. The options used are shown in Table 4-7.

4.2.2 Results and Discussion

The results of running PHREEQE and EQ3 with both the PREPHR and DEQPAK7 data sets are given in Tables 4-6 through 4-10, and discussed in this section.

Alkalinity and carbonate species: Table 4-6 shows the carbonate species concentrations calculated by each code using the two thermodynamic data sets and both the total alkalinity and total dissolved carbonate input options. Calculated values of log P CO_2 and of $SI_{calcite}$ (= log ($IAP_{calcite}/KT_{calcite}$)) which are sensitive to carbonate species ion activities are also shown.

Analytical data from Nordstrom and others (1979, Tab. III) are given in the first two columns of Table 4-6. According to Plummer (written communication, Nov. 1981) the total carbonate and carbonate species concentrations were calculated from analyzed titration alkalinity and pH values for sea water, using apparent constants for the carbonate system in sea water as is common practice among marine chemists.

For each test run, the total carbonate value calculated when alkalinity is entered is not identical with that given by Nordstrom and others. Likewise, when the Nordstrom and others total carbonate values are entered, the calculated alkalinity values do not agree with the analyzed value. This is because neither the PREPHR nor the DEQPAK7 data bases include carbonate system equilibrium constants with exactly the same values as those used to arrive at the concentrations given by Nordstrom and others.

A similar comparison obtained using WATEQF is also given by Nordstrom and others (1979, Tab. XII). The results given by them are the same as obtained here using the PHREEQE and the PREPHR data base, as they should be because the PREPHR and WATEQF data bases are closely similar.

The results of the last two pairs of columns in Table 4-6 were obtained using DEQPAK7 data with both codes. The results from the two codes agree within a few thousandths - differences due to activity coefficient formulation inconsistencies between the codes, rather than to any fundamental difference.

Aqueous species distribution and mineral saturation indices: A number of runs were made to compare the aqueous species distributions calculated by each code with the two data sets, and for comparison with distributions calculated by other codes and published by Nordstrom, and others (1979, Tab. VI and VII). The distribution of selected major ion species is given in Table 4-8, and of selected minor ion species in 4-9, both presented as negative log molalities. Saturation indices ($SI_{mineral}$ = log (IAP/KT)) of selected minerals resulting from the calculated aqueous species distributions are given in Table 4-10. The sources of data in the numbered columns are described in Table 4-7.

Table 4-6: Calculated Distribution of Carbonate Species Using Alkalinity and Total Carbonate Input Options. Activity Coefficients Calculated Using WATEQ Debye Huckel Expression for PREPHR Data and Debye Huckel BDOT Expression for DEQPAK7 Data. See Section 3.2.3).

	Analytical Data 1/		Code and Thermodynamic Data Set					
	mg/kg soln (ppm)	mm/kg H_2O (molality x10^3)	PHREEQE		PHREEQE		EQ3	
			---millimol/kg H_2O---					
			PREPHR DATA		DEQPAK7 DATA		DEQPAK7 DATA	
Total Inorganic Carbon as HCO_3^-	123.377	2.095	2.137	INPUT	2.175	INPUT	2.171	INPUT
H_2CO_3		0.012	0.012	0.011	0.014	0.014	0.012	0.012
2/ HCO_3^-		1.859	1.909	1.873	1.928	1.858	1.929	1.859
2/ CO_3^{-2}		0.224	0.216	0.211	0.232	0.224	0.232	0.224
Total Alkalinity as HCO_3^-	141.682	2.4066 3/	INPUT	2.362	INPUT	2.319	INPUT	2.322
log P CO_2 (atm)	----------		-3.39	-3.40	-----	-----	-3.34	-3.36
SI-Calcite	----------		0.741	0.732	0.812	0.796	0.813	0.798

1/ From Nordstrom and others, 1979, Table III.

2/ Total species concentrations including that paired with other ions.

3/ From reported total titration alkalinity of 2.322 mg/kg soln and factor 1.03643 kg soln/kg H_2O.

00065

0629

The important factors giving rise to the differences among the comparison results in columns 3 through 7 are:

- o The code used, whether PHREEQE or EQ3
- o The thermodynamic data base used, whether PREPHR or DEQPAK7; and
- o The activity coefficient expression used.

The results in column 3 were obtained using total alkalinity, rather that total carbonate as input. The effect of this selection on carbonate speciation was discussed in the preceeding section. Its effects on other aqueous species, the subject of this section, are negligible. The results in column 3 were from running PHREEQE as described in Table 4-7. They are identical with the results of Test Problem 1 of the original PHREEQE documentation (Parkhurst, Thorstensen and Plummer, 1980).

The number of digits shown in the results in Tables 4-8, 4-9, and 4-10 and similar tables in succeeding test problems was chosen for code comparison purposes, not to suggest levels of physical significance. The log molalities in Tables 4-8 and 4-9, for example, are given to three decimal places because it is at this level that differences between the codes, due to activity coefficient conventions and other second order effects, began to appear. Differences due to data base differences are much larger, as these results show.

Differences between columns 5 and 7 of Tables 4-8, 4-9, and 4-10, result only from the code used, whether PHREEQE or EQ3. With a few exceptions, values in columns 5 and 7 agree within 0.001 or 0.002 log units. More significant differences result from the different manner in which the two codes treat the activity of water itself and its products H^+ and OH^-, as described in section 3.2.1. This gives rise to the differences in H^+ and OH^- molalities in Table 4-8, and because of the importance of OH^- to its overall behavior, to the Al^{+3} molality in Table 4-9 and to the gibbsite and kaolinite saturation indices in Table 4-10.

Differences between columns 6 and 7 are due only to differences between the PREPHR and DEQPAK7 data sets, because the results in both columns were reached using the same code and the same dissolved ion

Table 4-7: Sources of Information in Columns 2 through 7 of Tables 4-8, 4-9, and 4-10.

	Activity Coefficient Expression (equation number in this report)	Dissolved Carbonate Input as:	Results in column of Tables 4-8, 4-9 and 4-10
Published WATEQF (upper) and WATEQ2 (lower) results from Nordstrom, and others, (1979); Tab. VI: Major species, Tab. VII: Minor species, and Tab. X: Saturation indices	Davies (3.2.7) d - 0.3	Total Alkalinity	2
Original published PHREEQE results with PREPHR data: (Parkhurst, Thorstenson, and Plummer 1980, Test Problem 1)	Davies (3.2.7) d - 0.3	Total Alkalinity	3
PHREEQE Code - PREPHR Data	Davies (3.2.7) d - 0.3	Total Alkalinity	3
PHREEQE Code - PREPHR Data	WATEQ Debye-Huckel (3.2.6)	Total Carbonate	4
PHREEQE Code - DEQPAK7 Data	Debye-Huckel (3.2.6)	Total Carbonate	5
EQ3 Code - PREPHR Data	Debye-Huckel (3.2.6)	Total Carbonate	6
EQ3 Code - DEQPAK7 Data	Debye-Huckel (3.2.6)	Total Carbonate	7

activity coefficient expression. As Table 4-8 shows, each data set includes data for essentially the same major ion species. It also shows that the differences between the two sets gives rise to calculated species molality differences most of which are less than 0.06 log units. This reflects the essential agreement which exists within the geochemical community about the identity and relative strength of major ion pairs.

Table 4-9 shows that the data set similarity does not extend to the minor ion species. The DEQPAK7 data set was intended for use in hydrothermal ore deposit work and so contains many more metallic elements and higher temperature (chloride) ion complexes than does PREPHR, which is intended for normal ground-water geochemical studies. Even where the same elements and species appear in both data sets, larger differences in the calculated molalities exist than in the major ion species. This reflects the greater uncertainty about minor ion complex identities and strengths.

Columns 4 and 5, and 6 and 7 of Table 4-10 show that the mineral saturation indices calculated using the two data sets have considerable disparities between them. This results in part from differences in the ion species activities, as suggested by the molality differences in Tables 4-8 and 4-9. More of the difference is due to different mineral equilibrium constant (log K) values in the two data sets. This is in keeping with the generally acknowledged fact that mineral equilibrium constants are among the least well known geochemical parameters. The effects of these uncertainties are shown in more detail in Sections 4.3 and 4.5, below.

Differences among values in columns 3, 4, and 6 of Tables 4-8, 4-9, and 4-10 show the effects of choosing various activity coefficient expressions. As Figures 3.2.1 and 3.2.2 show, disagreement among various activity coefficient equations is proportional to solution ionic strength, so that they will be larger in solutions more concentrated than sea water and will decrease in more dilute solutions.

Table 4-8: Negative Log Molalities (pm) of Selected Major Species in Full Sea Water Test Problem. For Detailed Column Heading Information See Table 4-7.

SPECIES	WATEQF/ WATEQ2 (2)	ORIGINAL PHREEQE (3)	NEW PHREEQE PREPHR (4)	NEW PHREEQE DEQPAK7 (5)	EQ3 PREPHR (6)	EQ3 DEQPAK7 (7)
Ca^{+2}	2.024	2.024	2.024	2.028	2.021	2.028
$CaSO_4^o$	2.939	2.938	2.938	2.925	2.979	2.923
$CaHCO_3^+$	4.481 4.449	4.482	4.491	4.224	4.281	4.223
$CaCO_3^o$	4.649 4.616	4.650	4.658	4.531	4.640	4.529
Mg^{+2}	1.312	1.312	1.312	1.320	1.314	1.320
$MgSO_4^o$	2.235 2.222	2.222	2.222	2.172	2.222	2.170
$MgHCO_3^-$	2.655 3.624	3.659	3.667	3.544	3.417	3.543
$MgCO_3^o$	4.045 4.014	4.048	4.056	3.931	4.012	3.929
Na^+	0.320	0.320	0.320	0.332	0.322	0.332
$NaSO_4^-$	2.178 2.195	2.195	2.195	2.217	2.060	2.216
$NaHCO_3^o$	3.785 3.752	3.785	3.794	-----	3.808	-----
$NaCO_3^-$	-----	4.183	4.191	4.473	4.019	4.472
K^+	1.983	1.983	1.983	1.983	1.986	1.983
KSO_4^-	3.767	3.763	3.763	3.744	3.605	3.743
Cl^-	0.247	0.247	0.247	0.258	0.247	0.258
SO_4^{-2}	1.810	1.808	1.808	1.821	1.877	1.822
HCO_3^-	2.825 2.836	2.826	2.834	2.820	2.894	2.820
CO_3^{-2}	4.422 4.566	4.422	4.431	4.362	4.447	4.364
F^-	4.410	4.410	4.368	4.415	4.540	4.415
MgF^+	4.442	4.442	4.491	4.453	4.337	4.452
Sr^{+2}	4.016	4.016	4.016	4.016	4.016	4.016
H_4SiO_4	4.145	4.145	4.145	4.159	4.152	4.159
H^+	8.093	8.093	8.098	8.098	8.126	8.125
OH^-	5.660	5.660	5.570	5.610	5.609	5.588
Ionic Strength	0.680	0.680	0.680	0.664	0.675	0.663
Activity H_2O	-----	0.9805	0.9805	0.9808	0.9814	0.9814

Table 4-9: Negative Log Molalities (pm) of Selected Minor Species in Full Sea Water Test Full Sea Water Test Problem. For Column Heading Information See Table 4-7.

SPECIES	WATEQF/ WATEQ2 (2)	ORIGINAL PHREEQE (3)	NEW PHREEQE PREPHR (4)	NEW PHREEQE DEOPAK7 (5)	EQ3 PREPHR (6)	EQ3 DEOPAK7 (7)
Mn^{+2}	8.654	8.657	8.621	9.296	8.728	9.298
$MnCl^{+}$	8.880	8.901	8.982	-----	8.793	-----
$MnCO_3^{o}$	-----	-----	-----	8.493	-----	8.493
Fe^{+3}	17.897	17.899	17.936	17.538	18.196	17.541
$Fe(OH)_2^{+}$	-----	8.157	8.157	9.157	8.120	9.158
$Fe(OH)_3^{o}$	8.071	8.070	8.071	-----	8.229	-----
$Fe(OH)_4^{-}$	7.664	7.664	7.664	7.439	7.626	7.439
Cu^{+2}	10.153	-----	-----	9.057	-----	9.057
$CuOH^{+}$	-----	-----	-----	7.983	-----	7.983
$Cu(OH)_3^{o}$	7.985	-----	-----	-----	-----	-----
$CuCO_3^{o}$	9.070	-----	-----	-----	-----	-----
Ag^{+}	14.394	-----	-----	14.755	-----	14.753
$AgCl_4^{-3}$	9.684	-----	-----	9.520	-----	9.521
Zn^{+2}	7.547	-----	-----	7.340	-----	7.341
$ZnCl^{+}$	-----	-----	-----	7.798	-----	7.798
$ZnCO_3^{o}$	7.894	-----	-----	-----	-----	-----
Al^{+3}	15.956 16.091	15.964	16.001	15.844	15.259	15.936
$Al(OH)_3^{o}$	----- 7.665	8.537	8.538	-----	8.694	-----
$Al(OH)_4^{-}$	7.115 7.259	7.131	7.131	7.114	7.126	7.114
Pb^{+2}	11.335	-----	-----	13.757	-----	13.750
$PbCl^{+}$	-----	-----	-----	13.171	-----	13.172
$PbCl_2^{o}$	11.017	-----	-----	13.623	-----	13.622
$PbCO_3^{o}$	9.743	-----	-----	9.602	-----	9.602
UO_2^{+2}	-----	15.500	15.476	16.484	-----	16.479
$UO_2(CO_3)_2^{-2}$	-----	8.736	8.728	9.572	-----	9.566
$UO_2(CO_3)_3^{-4}$	-----	7.902	7.903	7.851	-----	7.851
PO_4^{-3}	10.480	10.481	9.865	9.285	10.039	9.288
HPO_4^{-2}	6.988	6.988	6.750	6.195	6.916	6.195
$H_2PO_4^{-}$	8.381	8.381	8.382	7.784	8.545	7.782

Table 4-10: Saturation Indices (log(IAP/KT)) of Selected Minerals in Full Sea Water Test Problem. For Detailed Column Heading Information See Table 4-7.

NAME	COMPOSITION	WATEQF/ WATEQ2 (2)	ORIGINAL PHREEQE (3)	NEW PHREEQE PREPHR (4)	NEW PHREEQE DEOPAK7 (5)	EQ3 PREPHR (6)	EQ3 DEOPAK7 (7)
Calcite	$CaCO_3$	+ 0.74 + 0.74	+ 0.74	+ 0.73	+ 0.80	+ 0.67	+ 0.80
Dolomite	$CaMg(CO_3)_2$	+ 2.33 + 2.39	+ 2.33	+ 2.31	+ 3.42	+ 2.22	+ 3.42
Siderite	$FeCO_3$	- 9.00 - 8.97	- 9.01	- 9.02	- 6.41	- 9.33	- 6.40
Rhodochrosite	$MnCO_3$	- 3.73 - 3.70	- 3.88	- 3.97	- 4.46	- 4.10	- 4.46
Gypsum	$CaSO_4\ 2H_2O$	- 0.44 - 0.35	- 0.35	- 0.35	- 0.40	- 0.46	- 0.40
Celestite	$SrSO_4$	- 0.61	- 0.61	- 0.82	- 0.87	- 0.89	- 0.86
Hydroxyapatite	$Ca_5(PO_4)_3OH$	+ 0.60 + 0.67	+ 0.67	+ 0.48	-----	+ 0.04	-----
Fluorite	CaF_2	- 0.74	- 0.74	- 0.84	- 0.89	- 1.13	- 0.88
Hematite	Fe_2O_3	+15.23	+15.22	+15.22	+16.40	+14.74	+16.40
Gibbsite	$Al(OH)_3$	- 1.68 - 1.82	- 1.24	- 1.24	- 0.24	- 1.46	- 0.33
Quartz	SiO_2	- 0.05	- 0.05	- 0.05	- 0.16	- 0.13	- 0.16
Kaolinite	$Al_2Si_2O_5(OH)_4$	- 2.11	- 2.13	- 2.13	- 0.30	- 2.73	- 0.48
Sepiolite	$Mg_2Si_3O_{7.5}(OH).3H_2O$	+ 1.06 + 1.03	+ 1.04	+ 1.04	+ 2.42	+ 0.88	+ 2.43
Uraninite	UO_2	-----	-20.20	-20.18	-20.23	-----	-20.22

Finally, comparison of column 2 of Tables 4-8, 4-9, and 4-10, with the remaining columns illustrates how results of PHREEQE and EQ3 runs with both data sets and various activity coefficient expressions match with other aqueous speciation code results. The results shown are from the codes WATEQF and WATEQ2. WATEQF is one of the more widely used aqueous speciation codes, and in some ways is a predecessor to PHREEQE. WATEQ2, although written in the PL-1 language and so less widely useful than WATEQF, has associated with it a relatively large data base.

Agreement between WATEQF/WATEQ2 results with those made using the PREPHR data base is generally good, which is not surprising as much of the PREPHR data were taken from the WATEQF and WATEQ2 data bases. There is frequent disagreement of up to several log units between WATEQF/WATEQ2 minor element species results and those of the DEQPAK7 runs, however. As mentioned above, this is an honest reflection of the lack of geochemical knowledge of not only the strength but even of the identity of minor ion aqueous species.

4.3 TEST PROBLEM 3: DISSOLVE MICROCLINE IN DILUTE HCl.

The potassium feldspar microcline ($KAlSi_3O_8$) is a common rock-forming mineral which dissolves incongruently in pure water and dilute acids at 25 C. Minerals which may precipitate during the course of microcline dissolution include gibbsite ($Al(OH)_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), and muscovite ($KAl_3Si_3O_{10}(OH)_2$).

This problem simulates the dissolution of microcline in dilute (pH=4) HCl in order to illustrate and compare the reaction path modeling and phase boundary locating capabilities of PHREEQE and EQ3/EQ6. The system is a simple one with only potassium, aluminum, silica, and water involved in the reactions. Thus the simulated solution compositions at the mineral phase boundaries during the dissolution process can be compared with hand-calculated phase diagrams for code verification purposes.

The results of three simulations are described here. To compare the operation of the codes, independent of the data bases, the problem was run using DEQPAK7 data with both the PHREEQE and EQ3/EQ6 codes. To illustrate the effects on such a simulation of data base differences, the problem was run a third time using PREPHR data and the PHREEQE code.

4.3.1 Input

To simulate a reaction path with either code requires that an initial solution composition be specified. That was done here by fixing pH=4 and requiring that the codes add Cl^- for electrical neutrality. Both PHREEQE and EQ3 calculated a final Cl^- molality of 1.0115E-03, thus verifying the proper operation of the routines in each which achieve electro-neutrality by ion addition or subtraction.

The dissolution of microcline involves no oxidation-reduction reactions. Thus consideration of redox reactions was suppressed in running both codes.

The problem specifies consideration of only gibbsite, kaolinite, and muscovite, in addition to microcline. Thus quartz (SiO_2) an

additional possible mineral product of microcline dissolution, was suppressed in the EQ6 input and not included in the MINERALS input to PHREEQE.

The operation of EQ6 is straightforward. Given the initial solution composition as calculated by EQ3, it incrementally adds microcline. After each increment, it checks for solution saturation with respect to each active (not suppressed, as was quartz) mineral in its data base. When a supersaturated mineral or minerals are noted, the last increment size is reduced so as to better define the total quantity of microcline required to reach the phase boundary. The newly saturated mineral is then added to the problem defining matrix and the amount of microcline solution required for its saturation found directly by solution of that matrix. From that point, incremental addition resumes until either another phase boundary is reached or the reacting mineral (here microcline) saturates or is exhausted. Thus EQ6 both defines and locates phase changes which occur during a reaction path with only the starting solution and reactant species defined by the user.

PHREEQE, on the other hand, requires greater user input to perform a reaction path simulation. Like EQ6, PHREEQE calculates the extent of reaction progress required to reach a given phase boundary, along with the amount of mass transfer (moles of minerals dissolved or precipitated) during the reaction and the solution composition at the phase boundary. Unlike EQ6, though, PHREEQE does not itself determine the mineral assemblages occuring at the phase boundaries crossed during a reaction path simulation, but requires user input to define these assemblages.

Test problem 5 in the PHREEQE documentation (Parkhurst, Thorstensen, and Plummer, 1980) is a simulation of microcline dissolution in a neutral (pH=7) pure water, and very closely resembles this test problem. The detailed procedure by which PHREEQE is used for reaction path simulations is described there and therefore is not repeated here.

4.3.2 Results and Discussion

This problem was used both for code and for data base comparisons, and the results of each will be discussed.

Code Comparison: The results of PHREEQE and EQ6 simulations using DEQPAK7 data are given in table 4-11. The output values listed for comparison purposes include various ion molalities, activities and activity ratios, mineral saturation indices, the extent of reaction progress (moles of microcline dissolved) and the quantity of other minerals precipitated during the incongruent dissolution. PHREEQE calculations were made only for the phase boundaries so only EQ6 results for the intermediate points at even values of reaction progress are given.

The simulation predicts that after 14.4 micromoles (μmol) of microcline dissolve congruently, the system becomes saturated with respect to gibbsite at point (A). Microcline dissolution is now incongruent:

$$KAlSi_3O_8 + H_2O + H^+ = Al(OH)_3 + K^+ + 3\ SiO_{2(aq)}. \qquad (4.3.1)$$

and proceeds until a total of 18.9 μmols microcline have dissolved, and the system becomes saturated with kaolinite at point (B). Incongruent dissolution continues, by the overall reaction:

$$KAlSi_3O_8 + 2\ Al(OH)_3 + H^+ = \frac{3}{2}\ Al_2Si_2O_5(OH)_4 + K^+ + \frac{1}{2}\ H_2O_{(aq)} \qquad (4.3.2)$$

until, when a total of 22.15 μmols microcline have been dissolved, gibbsite is no longer saturated (C). The continuing reaction is now incongruent only with respect to kaolinite:

$$KAlSi_3O_8 + \frac{1}{2}\ H_2O + H^+ = \frac{1}{2}\ Al_2Si_2O_5(OH)_4 + K^+ + 2\ SiO_{2(aq)} \qquad (4.3.3)$$

After a total of 102.8 μmols microcline dissolution, the solution becomes saturated also with muscovite (E). The reaction then proceeds:

$$KAlSi_3O_8 + Al_2Si_2O_5(OH)_4 = KAl_3Si_3O_{10}(OH)_2 + 2SiO_{2(aq)} + H_2O \qquad (4.3.4)$$

until a total of 150.0 μmols microcline have dissolved, and the system reaches equilibrium with the reactant microcline (F).

Table 4-11: PHREEQE and EQ6 Results for Test Problem 3 With DEOPAK7 Data.

CODE	SYSTEM STATE 1/	Microcline dissolved (μ moles)	log Total Molality K^+	Al^{+3}	SiO_2	pH	$\log \frac{a_{K^+}}{a_{H^+}}$
EQ6		1.000	-6.0000	-6.0000	-5.5228	4.0169	-1.9882
EQ6		10.000	-5.0000	-5.0000	-4.5229	4.2038	-0.8019
EQ6	Reach Gibbsite (A)	14.443	-4.8403	-4.8403	-4.3632	4.3305	-0.5157
PHREEQE	Saturation	14.365	-4.8427	-4.8427	-4.3656	4.3292	-0.5194
EQ6	Reach Kaolinite Continue Gibbsite (B)	18.932	-4.7228	-4.8753	-4.2457	4.3432	-0.3854
PHREEQE	Saturation	18.931	-4.7228	-4.8783	-4.2457	4.3421	-0.3866
EQ6	End Gibbsite, Continue Kaolinite (C)	22.129	-4.6550	-4.9017	-4.2456	4.3528	-0.3080
PHREEQE	Saturation	22.176	-4.6541	-4.9051	-4.2457	4.3518	-0.3081
EQ6	Cont. Kaolinite Satn (D)	100.000	-4.0000	-9.0286	-3.6990	5.9243	1.9193
EQ6	Reach Muscovite, Continue Kaolinite (E)	102.827	-3.9879	-8.3070	-3.6869	7.4137	3.4207
PHREEQE	Saturation	102.820	-3.9879	-8.3958	-3.6869	7.4138	3.4208
EQ6	Reach Microcline, Muscovite, Kaolinite (F)	149.958	-3.9852	-8.4735	-3.5230	7.4110	3.4207
PHREEQE	Saturation	149.950	-3.9852	-8.5623	-3.5230	7.4111	3.4207

1/ Letter identifies point on Figure 4-1.

Table 4-11: (Continued)

$\log \frac{a_{Al^{+3}}}{a_{H^+}^3}$	$\log a_{SiO_2}$	Precipitated Mineral (μmoles)			Saturation Indices			
		Gibbsite	Kaolinite	Muscovite	Gibbsite	Kaolinite	Muscovite	Microcline
5.9317	-5.5228	---	---	---	-2.0286	-6.6115	-15.3261	-12.7082
7.4532	-4.5229	---	---	---	-0.5071	-1.5685	-6.5753	-7.0005
7.9603	-4.3632	0.000	---	---	0.0000	-0.2350	-4.2890	-5.7283
7.9602	-4.3656	0.000	---	---	0.0000	-0.2397	-4.2997	-5.7390
7.9603	-4.2457	5.603	0.002	---	0.0000	0.0000	-3.8061	-5.2454
7.9603	-4.2457	5.697	0.000	---	0.0000	0.0000	-3.8073	-5.2466
7.9603	-4.2456	0.000	4.794	---	0.0001	0.0000	-3.7288	-5.1680
7.9603	-4.2457	0.000	4.868	---	0.0000	0.0000	-3.7288	-5.1681
7.4137	-3.6991	---	50.000	---	-0.5466	0.0000	-1.5014	-1.8475
7.4045	-3.6899	---	51.411	0.000	-0.5558	0.0000	0.0000	-0.3277
7.4047	-3.6899	---	51.408	0.000	-0.5558	0.0000	0.0000	-0.3278
7.2406	-3.5260	---	5.254	46.480	-0.7197	0.0000	0.0000	0.0000
7.2408	-3.5261	---	5.245	46.486	-0.7196	0.0000	0.0000	0.0000

The agreement between the two sets of results in table 4-11 is excellent and clearly demonstrates that both codes are capable of giving the same results when used with the same data base. The largest differences evident are between the Al^{+3} total molality values. As in the previous, sea water, test problem, these differences can be attributed to the differing expressions for water activity in the two codes.

Data-base Comparison: The phase relationships in systems such as that being modeled in this problem can be conveniently displayed in activity-activity diagrams (Helgeson, Brown, and Leeper, 1969). Figure 4-1 shows stability fields of the minerals considered in this problem with boundaries calculated using mineral equilibrium data from both the PREPHR (dashed lines) and DEQPAK7 (solid lines) data bases. This figure shows that there are significant differences between the data bases for these minerals, and that the PREPHR data predicts a wider range of stability for kaolinite and muscovite than does the DEQPAK7 data.

The positions of the several points calculated during the reaction path simulations are also shown on figure 4-1. The points labeled A through F were calculated by the PHREEQE and EQ6 simulations using DEQPAK7 data and are given in table 4-11. The coincidence of points B and C with the hand-calculated gibbsite-kaolinite phase boundary, of E with the kaolinite-muscovite boundary, and of F with the kaolinite, muscovite, microcline triple point provides verification that the phase boundary location portions of both codes are operating correctly.

The differences between PREPHR and DEQPAK7 data which give rise to the two sets of phase boundaries in figure 4-1 also cause differences in the amount of reaction progress and mass transfer calculated and in the reaction path itself when each is used in simulation modeling. The results of simulating microcline dissolution using PHREEQE and PREPHR data, are given in table 4-12 and are considerably different from those from using PHREEQE andd DEQPAK7 data shown in table 4-11, and repeated in part in table 4-12.

In the PREPHR based simulation, the system never becomes saturated with gibbsite, but instead reaches kaolinite saturation after 9.2 μmols microcline have dissolved at point (1). Incongruent solu-

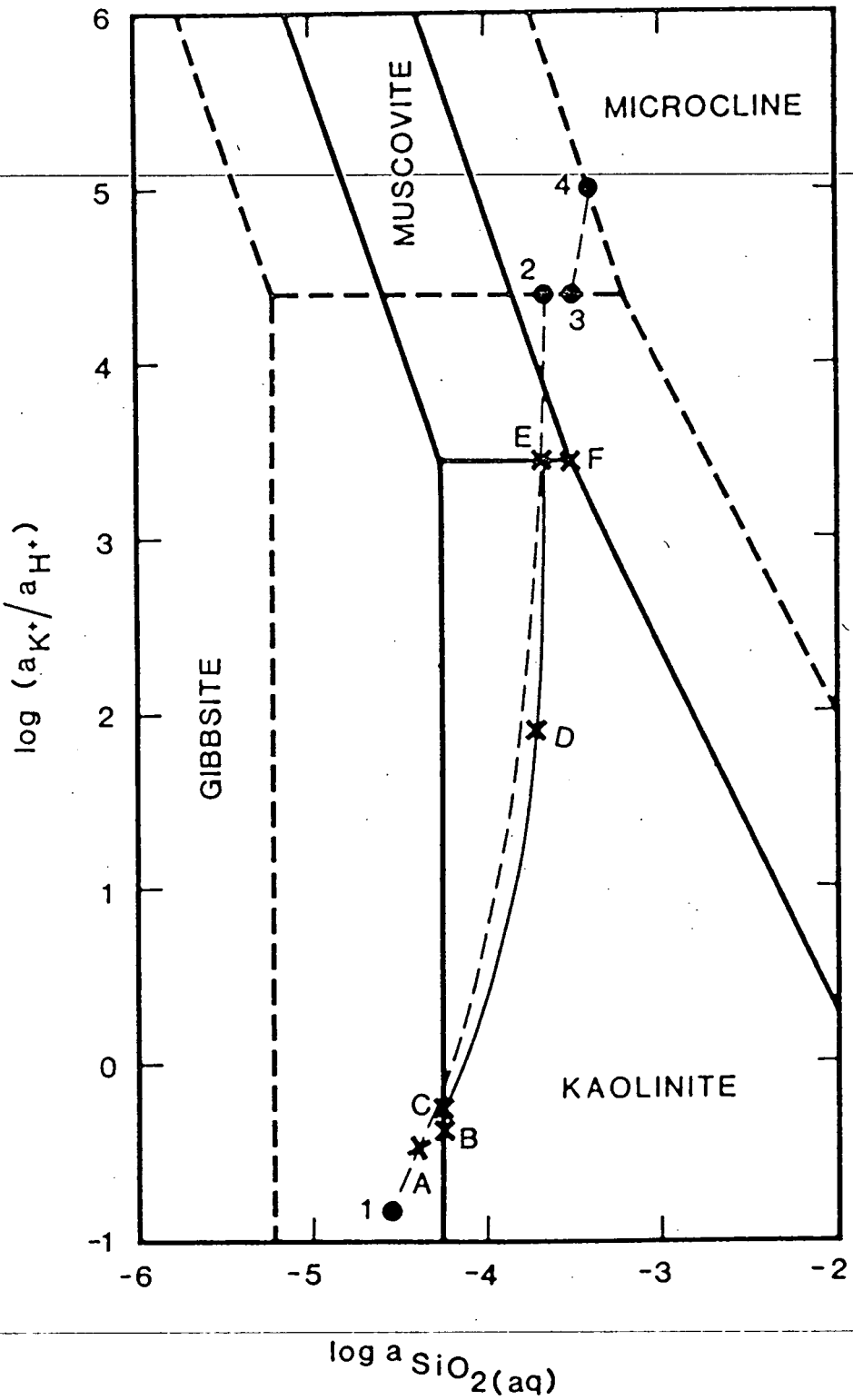

Figure 4-1: Variation of Iron and Uranium Chemistry with Reactions Progress in Test Problem 4. Letters Correspond to Points Described in Table 4-15.

Table 4-12: Test Problem 3 Results Using Both PREPHR and DEOPAK7 Data in PHREEQE

DATA SET	SYSTEM STATE 1/	Microcline dissolved (μ moles)	pH	$\log \frac{a_{K^+}}{a_{H^+}}$	$\log \frac{a_{Al^{+3}}}{a_{H^+}^3}$	$\log a_{SiO_2}$	SATURATION INDICES Gibbsite	Kaolinite	Muscovite	Microcline
PREPHR	Reach Kaolinite Saturation	(1) 9.222	4.1879	-0.8529	7.4121	-4.5580	-0.6370	0.0000	-5.2609	-7.990
PREPHR	Reach Muscovite	(2) 109.577	8.3736	4.4080	6.5254	-3.6713	-1.5237	0.0000	0.0000	-0.9556
DEQPAK7	Continue Kaolinte Saturation	(E) 102.820	7.4138	3.4208	7.4047	-3.6899	-0.5558	0.0000	0.0000	-0.3278
DEQPAK7	Reach Microcline, Muscovite, Kaolinite Saturation	(F) 149.950	7.4111	3.4207	7.2400	-3.5261	-1.7196	0.0000	0.0000	-0.0000
PREPHR	End Kaolinite Continue Muscovite Saturation	(3) 168.788	8.3621	4.4080	6.3374	3.4834	-0.7116	0.000	0.0000	-0.5797
PREPHR	Reach Microcline, Muscovite Saturation	(4) 216.752	8.8744	5.0282	6.0474	-3.4003	-2.0015	-0.4135	0.0000	0.0000

1/ Letters and numbers identify points in Figure 4-1.

080000

0629

tion begins according to reaction 4.3.3 and continues until, after 109.6 μmols microcline have dissolved, the solution becomes saturated with muscovite as well point (2). This is the same stage of reaction progress as point (E) of the DEQPAK7 based simulation, although because of the data base difference, E was reached after 102.8 μmol microcline dissolution and corresponds to a different aqueous phase composition, as shown in Table 4-12 and Figure 4-1.

From point (2), incongruent dissolution continues according to reaction 4.3.4, until, when 168.8 μmol microcline have dissolved, kaolinite is no longer saturated (3). This is a significant departure from the DEQPAK7 based simulation in which the reaction ended at saturation after dissolution of only 150.0 μmol microcline.

Dissolution incongruent with respect to muscovite continues from point 3:

$$KAlSi_3O_8 + \frac{2}{3} H^+ = \frac{1}{3} KAl_3Si_3O_{10}(OH)_2 + \frac{2}{3} K^+ + 2\ SiO_{2(aq)} \quad (4.3.5)$$

until a total of 216.8 μmol microcline have dissolved at which point the solution reaches saturation with respect to microcline and the reaction stops at point (4).

As Table 4-12 shows, the compositions of the aqueous phase calculated at microcline saturations from the two data bases are quite different. The difference is also shown on Figure 4-1 where both sets of reaction simulation points are plotted on the phase diagram.

4.4 TEST PROBLEM 4: REDUCE AN OXYGENATED, CALCITE AND HEMATITE SATURATED SOLUTION BY ADDING METHANE.

The previous test problem illustrated the ability of each code to simulate an incongruent mineral dissolution path which did not involve redox reactions. Redox reactions are particularly difficult to simulate because of the occurrence of very large changes in oxidation state (described as f_{O_2} or pe, for example) as one redox species gains dominance over another.

This problem has been designed to demonstrate the ability of each code to simulate reaction paths which include redox reactions, and was chosen less for its resemblance to any real problem the codes might face than for the radical oxidation state changes it demands. The problem is in several steps:

- Simulate a starting solution saturated with respect to calcite ($CaCO_3$) and hematite (Fe_2O_3), and with fixed sodium, uranium, sulfate, and chloride concentrations. This solution is open to a gas phase with fixed partial pressures of O_2 and CO_2.
- The starting solution, now no longer open to the O_2 and CO_2 containing gas phase, is reduced by the addition of methane (CH_4) to it. During this reduction, the solution maintains saturation with calcite. The system is assumed to contain 0.1 mmol hematite per kilogram water, and the solution stays in equilibrium with that hematite until it has entirely dissolved. Finally, it is assumed that the minerals uraninite (UO_2) and pyrite (FeS_2) will precipitate should the solution become supersaturated with respect to them.

4.4.1 Input: Starting Solution

The initial solution was specified by combining fixed input molalities of some dissolved species with mineral equilibria control on others and gas partial-pressure specifications on the remainder. The solution pH was also calculated to satisfy electroneutrality.

Input in this form illustrates the ability of the solution speciation routine in PHREEQE and in EQ3 to accept various types of input data.

Table 4-13 shows the input data used and relates the mineral and gas equilibria to the species they define. For EQ3, only these data (plus a starting estimated pH of 7.4) were required to directly simulate the starting solution. With PHREEQE, additional required starting estimates were taken as: pH=7.4; pe=13.2; calcium=1.5 E-03 and total carbonate=3.0 E-03.

4.4.2 Results: Starting Solution

The starting solution composition calculated by each code is given in Table 4-14, and other properties of this solution in the first two lines of Table 4-15. No differences between their results exceed 0.004 log units, an error far smaller than likely to be associated with any thermodynamic data set or water analysis. These results show the ability of both codes to simulate solution compositions given mineral equilibria and gas partial pressure constraints, and to adjust pH for electroneutrality.

4.4.3 Input: Reaction Simulation

Reaction path simulation using PHREEQE requires that points of interest along the path be specified by the user, following which, the code calculates the amount of mass transfer in the system from point to point along the path. It is therefore necessary to describe here the logic by which the reaction path was specified.

The starting solution is oxidizing, by virtue of its exposure to an oxygen-bearing gas phase. The reactant, methane, is reducing and will tend to lower the oxidation potential of the solution as it is added. The reaction by which methane is oxidized, and hence reduces other species in solution can be written:

Table 4-13: Initial Solution for Test Problem 4.

Species	Specified by:
Sodium	Input at 7.0 E-03 molal
Calcium	Calcite ($CaCO_3$) saturation
Iron	Hematite (Fe_2O_3) saturation
Uranium	Input at 4.0 E-05 molal
Carbonate	Input P_{CO2} of 0.01 atmosphere
Sulfate	Input at 1.0 E-03 molal
Chloride	Input at 5.0 E-03 molal
Hydrogen (pH)	Solution electroneutrality
Oxygen (pE)	Input P_{O_2} of 0.2 atmosphere

Table 4-14: Calculated Compositions of Initial Solution for Test Problem 4 using EQ3 and PHREEQE with DEQPAK7 Data.

		EQ3	PHREEQE
Sodium*	(log molality)	- 2.155	- 2.155
Calcium	(log molality)	- 2.752	- 2.748
Iron	(log molality)	-16.304	-16.304
Uranium*	(log molality)	- 4.398	- 4.398
Carbonate	(log molality)	- 2.415	- 2.411
Sulfate*	(log molality)	- 3.000	- 3.000
Chloride*	(log molality)	- 2.301	- 2.301
pH	(units)	7.312	7.316
pe	(units)	13.289	13.285
Ionic Strength	(molality)	0.0128	0.0128
P_{CO_2}*	(atmospheres)	0.010	0.010
P_{O_2}*	(atmospheres)	0.200	0.200
Dissolved O_2	(log molality)	- 3.599	- 3.598

* Values fixed by input.

$$CH_4 + 3H_2O = CO_3^{-2} + 10H^+ + 8e^- \quad (4.4.1)$$

In addition to dissolved oxygen, the solution contains uranium, iron and sulfate which may also undergo redox reactions within the range of conditions found in natural waters. To specify the reaction path, it is necessary to decide:

i) the order in which dissolved elements will be reduced by the added methane; and

ii) whether, as a result of solution reduction, mineral phases will become saturated which, by their precipitation, will constrain the concentration of the solution.

The reduction reactions effecting oxygen, sulfate, iron, and uranium are:

$$O_2 + 4H^+ + 4e^- = 2H_2O \quad (4.4.2)$$

$$SO_4^{-2} + 8H^+ + 8e^- = S^{-2} + 4H_2O \quad (4.4.3)$$

$$Fe^{+3} + e^- = Fe^{+2} \quad (4.4.4)$$

$$UO_2^{+2} + 4H^+ + 2e^- = U^{+4} + 2H_2O \quad (4.4.5)$$

Minerals likely to be important in the system include:

Uraninite (UO_2), for which precipitation reactions can be written:

$$UO_2^{+2} + 2e^- = UO_2 \quad (4.4.6)$$

$$U^{+4} + 2H_2O = UO_2 + 4H^+ \quad (4.4.7)$$

Pyrite (FeS_2), for which precipitation reactions can be written:

$$Fe^{+3} + 2SO_4^{-2} + 16H^+ + 15e^- = FeS_2 + 8H_2O \quad (4.4.8)$$

$$Fe^{+2} + 2SO_4^{-2} + 16H^+ + 14e^- = FeS_2 + 8H_2O \quad (4.4.9)$$

The oxidized species first attacked by the added methane will be dissolved oxygen, because with it is associated the highest oxidation potential of any of the reactions 4.4.2 through 4.4.9. (Stumm and Morgan, 1981, Chapt. 7; Garrels and Christ, 1965). Before the oxidation potential of the system can drop into the region where the other reactions can become active, the initial 0.252 mmols of dissolved O_2 present (table 4-15) must be reduced. According to reaction 4.4.2, this will require 4*0.252=1.008 mmol e^-, which would be supplied by the oxidation of 1.008/8=0.126 mmol of methane by reaction 4.4.1.

The first reaction step with the PHREEQE simulation was therefore to add 0.126 mmol methane to the initial solution. Properties of the resulting solution are shown in Table 4-15 and in Figure 4-2. This solution is very little different from the initial solution, except for its much lower dissolved oxygen content. Addition of less than 10^{-6} mol methane to this solution will entirely deplete its dissolved oxygen thus shifting solution oxidation state control to one of the mineral precipitation reactions 4.4.6 or 4.4.8.

Because the uraninite saturation index (-22, Table 4-15) is considerably closer to zero (saturation) than that of pyrite (-238), it is not unreasonable to assume that uraninite saturation occurs next in the reaction path. The next simulation step was therefore to calculate the amount of methane addition required to reach uraninite saturation. This required 1.8E-07 moles of methane, for a total of 0.12618 mmol methane to reduce the initial solution to the point of uraninite saturation.

Properties of the solution at the first point of uraninite saturation (A) are given in Table 4-15 and in Figure 4-2. Comparison of these results with those of the previous point on the reaction path illustrate the large changes in solution property values which can accompany small steps in reaction progress in systems where redox reactions are occurring. Here, for example, a change in reaction progress of less than 2E-07 moles leads to a pe change of over 11 units (a dissolved oxygen change of 10^{44}), a change in

UO_2^{+2}/U^{+4} ratio of 10^{23} by reaction 4.4.5, a pyrite saturation index change of +167, and so forth. The ability of PHREEQE to track very sharp changes in solution state is thus demonstrated.

The assumption that uraninite saturates at a lower value of reaction progress than pyrite is also justified by the results at this step. As shown in table 4-15, at the first point of uraninite saturation, pyrite remains undersaturated, with a saturation index of -72.

With continuing methane addition, the solution will become more reducing and the next change in reaction path will occur at the point of pyrite saturation. As the next step in the simulation, the amount of methane needed to reduce the uraninite saturated solution to the point of pyrite saturation was calculated. 1.00 E-05 moles are required for a total of 0.1362 mmol methane added so far in the simulation.

The solution properties at the first point of pyrite saturation (B) are shown in Table 4-15 and Figure 4-2. The solution here has a lower oxidation potential (pe = -3.2) than at the previously simulated point of first uraninite precipitation (pe = 1.6), and so the equilibrium proportions of the redox reactions 4.4.1 through 4.4.5 have shifted toward the reduced species with the resulting lowering in the ratios of oxidized to reduced species given in Table 4.4.3. With the change in dominant uranium species from oxidized to reduced, the total dissolved uranium content decreases as uraninite precipitates. Likewise, the total iron content increases because of the increasing ability of hematite to dissolve:

$$Fe_2O_3 + 6H^+ + 2e^- = 2Fe^{+2} + 3H_2O \qquad (4.4.10)$$

as Fe^{+2} stability in the solution increases. Because pyrite is an Fe^{+2}-bearing solid, however, the total iron dissolved content stops increasing when pyrite saturates.

The system is now poised at the point where, as methane is added, hematite dissolves by such a reaction as 4.4.10, while pyrite precipitates by such a reaction as 4.4.9. This process will continue

Table 4-15: Comparison of PHREEQE and EQ6 Results for Test Problem 4.

CODE	SYSTEM STATE 1/	Extent of Reaction (millimoles CH_4 added)	pH	pe	Dis-solved oxygen (log mols)	Total iron (log mols)
EQ3	Starting solution: calcite and Hematite saturated at	-0-	7.312	13.289	- 3.599	-16.304
PHREEQE	P_{CO_2}=0.01 atm, P_{O_2}=0.02 atm	-0-	7.316	13.285	- 3.598	-16.304
PHREEQE	Exhaust initial dissolved O_2	0.126	7.279	12.633	- 6.354	-16.299
PHREEQE	Uraninite saturates; continuing (A)	0.1262	7.279	1.608	-50.4	-12.342
EQ6	calcite, hematite saturation	0.1284	7.274	1.550	-50.7	-12.278
EQ6	Pyrite saturates; saturated (B)	0.1358	7.269	- 3.201	-69.7	- 7.511
PHREEQE	calcite, hematite, uraninite	0.1362	7.272	- 3.205	->60	- 7.510
PHREEQE	Intermediate point	0.4362	7.327	- 3.295	->60	- 7.594
EQ6	Intermediate point	0.5000	7.338	- 3.314	-69.9	- 7.619
EQ6	Hematite exhausted; saturation (C)	0.5107	7.340	- 3.344	-70.0	- 7.982
PHREEQE	with calcite, uraninite, pyrite	0.5112	7.343	- 3.322	->60	- 7.617
EQ6	End of simulation	1.2000	7.340	- 4.227	-73.6	-17.628
PHREEQE		1.2112	7.344	- 4.236	->60	-17.590

1/ Letters refer to points in Figure 4-2.

Table 4-15: (Continued).

log molality ($\frac{Fe^{+3}}{Fe^{+2}}$)	Total uranium (log mols)	log molality ($\frac{UO_2^{+2}}{U^{+4}}$)	log molality ($\frac{Tot\ CO_3^{-2}}{CH_4}$)	log molality ($\frac{Tot\ SO_4^{-2}}{Tot\ S^{-2}}$)	Saturation Index: Hematite	Uraninite	Pyrite	Card Numbers in Figure 13-1
7.83	- 4.398	29.36	141.	139.	0.	- 23.	-248.	
7.80	- 4.398	29.40	>60	>60	0.	- 23.	-248.	1-32
7.10	- 4.398	29.00	>60	>60	0.	- 22.	-238.	33-45
-3.93	- 4.398	6.01	47.74	44.76	0.	0.	- 72.	46-58
-4.02	- 4.529	5.89	47.23	44.42	0.	0.	- 71.	
-8.77	-10.422	- 3.60	9.18	6.21	0.	0.	0.	
-8.78	-10.418	- 3.60	9.17	6.20	0.	0.	0.	59-73
-8.80	-10.364	- 3.71	8.94	5.97	0.	0.	0.	74-90
-8.68	-10.355	- 3.74	8.88	5.93	0.	0.	0.	
-8.70	-10.353	- 3.80	8.66	5.71	0.	0.	- 1.	
-8.68	-10.350	- 3.74	8.88	5.90	0.	0.	0.	74-90
-9.46	-10.355	- 5.48	1.59	- 0.49	-22.	0.	0.	
-9.46	-10.350	- 5.49	1.56	- 1.40	-22.	0.	0.	91-105

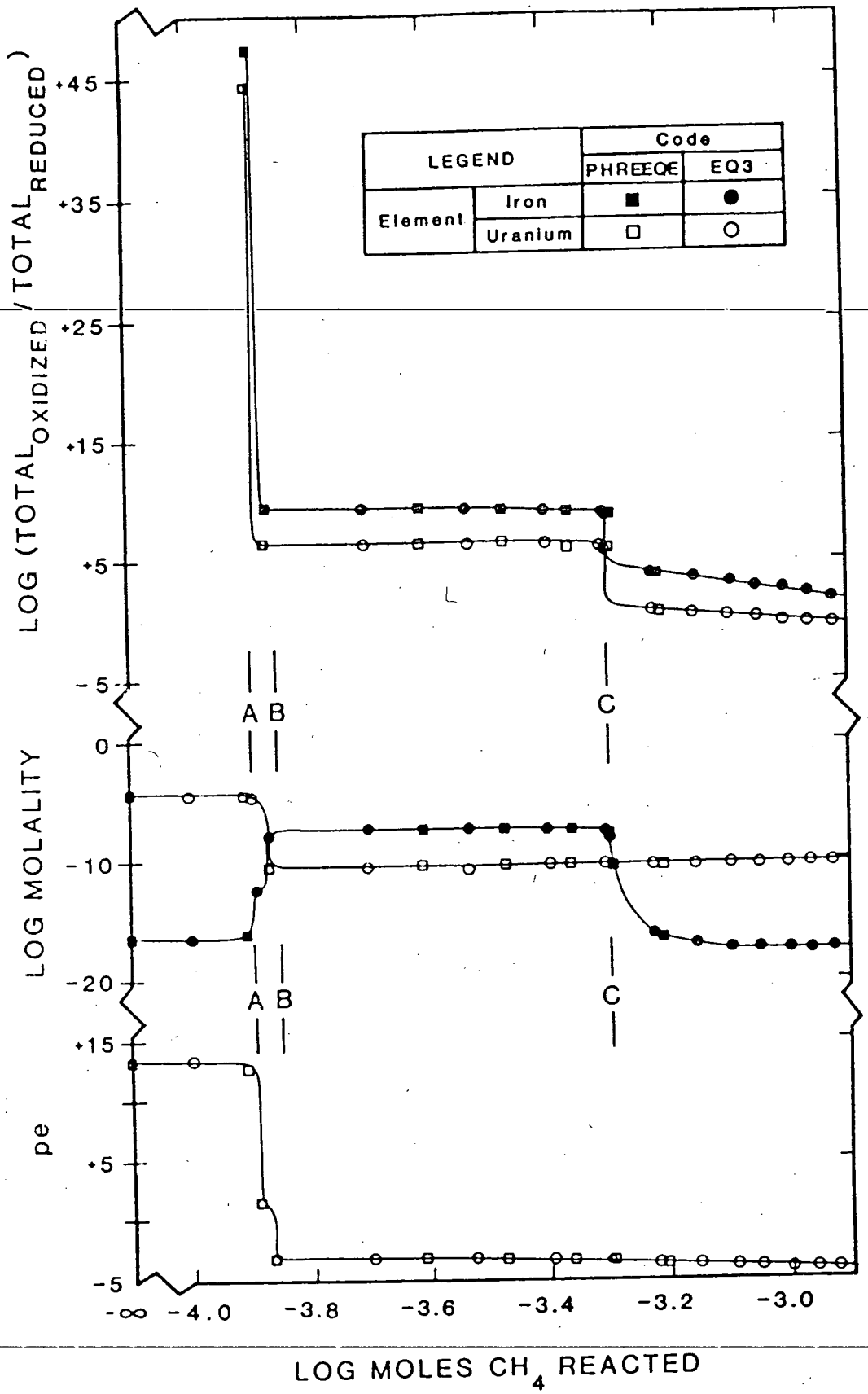

Figure 4-2: Activity Diagram for Gibbsite, Kaolinite, Muscovite and Microcline at 25 C. Dashed Lines PREPHR data; Solid Lines from DEOPAK7 data. Letters and numbers correspond to points in Tables 4-11 and 4-12.

until the 0.1 mmol hematite per kilogram solution specified in the problem description has been dissolved. The point of hematite exhaustion becomes the next one of change on the reaction path (C).

An overall reaction describing coupled hematite dissolution and pyrite precipitation can be written by combining reactions 4.4.9 and 4.4.10:

$$Fe_2O_3 + 4SO_4^{-2} + 38H^+ + 30e^- = 2FeS_2 + 19H_2O \qquad (4.4.11)$$

Thus, to dissolve 0.1 mmol hematite will require 3.0 m mol e^-. If these are supplied by reaction 4.4.1, 3.0/8=0.375 mmol methane will be needed.

The next calculation was then to simulate the mass transfer and solution composition resulting from the addition of 0.375 mmol methane to the calcite, uraninite, hematite, and pyrite saturated solution. Properties of this solution - to which a total of 0.5112 mmol methane have been added - are given in table 4-15, along with the properties of a solution to which an intermediate 0.4362 mmol methane were added. In spite of a relatively large methane addition, the solution properties change very little in this range because of the redox poising effect of the hematite-pyrite mineral pair.

The remaining simulation is to show the effects of continued methane addition to the system now no longer saturated with hematite. There is a gentle decrease in pe accompanying a decreased ratio of oxidized to reduced species concentrations. Because of uraninite saturation, the uranium content remains essentially constant. In the absence of dissolving hematite, the total iron content decreases as more pyrite precipitates due to increasing reduced sulfur (total S^{-2}) concentrations.

To simulate the behavior of this system with EQ6 does not require the definition of each point of interest on the reaction path, but only of the starting system description. That is, the EQ6 simulation required only the definition of the initial solution-from

the EQ3 run previously described, the specification that calcite and 0.1 mmol hematite were available as reactants, and that the reaction path would consist of the addition of a total of 1.2 mmol methane. With this input, the code itself determines what phases saturate or become exhausted, and at what values of reaction progress these system changes occur.

4.4.4 Results: Reaction simulation.

EQ6 simulation results are given in Table 4-15 and shown on Figure 4-2. These results are in excellent agreement with those of the PHREEQE simulation in terms both of the extents of methane addition required to reach the several phase boundaries, and of the calculated properties of the solutions at the boundaries and intermediate points. This agreement provides verification by code-to-code comparison of both the PHREEQE and EQ6 codes abilities to simulate reaction paths in systems including oxidation-reduction reactions.

4.5 TEST PROBLEM 5: CARBONATE AQUIFER DEDOLOMITIZATION BY GYPSUM SOLUTION WITH INCREASING TEMPERATURE.

The water in carbonate (limestone) aquifers is frequently saturated with respect to the minerals calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Certain carbonate aquifers also contain disseminated gypsum ($CaSO_4.2H_2O$). As the gypsum dissolves in the calcite-and dolomite-saturated solution, calcite precipitates which in turn leads to dolomite solution. As the dolomite originally present in the formation is replaced by calcite, the aquifer is said to have been dedolomitized. The overall reaction by which this occurs can be written:

Gypsum + Dolomite = 2 Calcite + Solution (4.5.1)

$$CaSO_4 \cdot 2H_2O + CaMg(CO_3)_2 = 2\ CaCO_3 + Mg^{+2}_{(aq)} + SO^{-2}_{4}\ (aq) + 2\ H_2O \qquad (4.5.2)$$

Dedolomitization frequently occurs with increasing depth in carbonate aquifers. As increasing depth is accompanied by increasing temperature, to simulate a natural dedolomitizing system requires that both the gypsum solution reaction and the accompanying temperature increase be simulated. This problem illustrates and compares the temperature changing capabilities of PHREEQE and EQ3/6 and also serves as an additional example of their reaction simulation capacities.

Like Problem 4, this simulation is in two steps:

- Simulate a starting solution saturated with respect to calcite and dolomite and at a fixed partial pressure of CO_2; and
- Simulate the reactions which accompany the addition of gypsum with an accompanying temperature increase to the starting solution.

Three simulations were run and the results are given here. The EQ3/EQ6 codes and PHREEQE were run with the DEQPAK7 data set to illustrate code comparability. In addition, PHREEQE was run with the PREPHR data set to illustrate the effects of thermodynamic data base changes on the results of this problem.

4.5.1 Input

The starting solution composition was specified by combining fixed input molalities of some dissolved species with mineral equilibria control on others and gas partial pressure specifications on the remainder. The solution pH was calculated by the codes in order to satisfy electroneutrality. Table 4-16 shows the input data used and relates the mineral and gas equilibria to the dissolved species they define.

No oxidation-reduction reactions are involved in the gypsum solution process being simulated so consideration of redox processes in the reaction simulations of EQ6 and PHREEQE were surpressed. For purposes of calculating the initial solution, though, a pe of 4.0 was specified. An initial solution pH estimate was also required and the value 7.0 was used both for EQ3 and PHREEQE.

The reaction path simulated began with the initial solution at 25 C and considered gypsum dissolution at a rate such that when 10 mmol gypsum had dissolved, a temperature of 75 C would have been reached. This was specified directly in the input to PHREEQE by making use of the "STEPS" and "TEMP" input options. For EQ6 it was specified by making temperature a function of reaction progress (XI):

$$t\ (\text{Celsius}) = 25.0 + 5.0\ E{+}03 * XI\ (\text{moles}) \qquad (4.5.3)$$

Using EQ6, the simulation was continued using the same temperature rise equation until gypsum saturation occurred in the solution and beyond to determine the temperature at which gypsum and anhydrite ($CaSO_4$) were in equilibrium. In PHREEQE, it is not possible to make temperature change a function of reaction progress in such a way that the code can be used to find a temperature at which a specified

Table 4-16: Initial Solution for Test Problem 5.

SPECIES	SPECIFIED BY
Sodium	Input at 1.0 E-03 molal
Calcium	Calcite ($CaCO_3$) saturation
Magnesium	Dolomite ($CaMg(CO_3)_2$) saturation
Carbonate	Input P_{CO_2} = 0.01 atmosphere
Sulfate	Input at 1.0 E-10 molal
Chloride	Input at 1.0 E-03 molal
Hydrogen (pH)	Solution electroneutrality
Oxygen (pe)	Input pe = 4.0. Redox reactions not considered during reaction simulation

equilibrium occurs. Thus, following the initial addition of 10 mmol gypsum and temperature rise to 75 C the PHREEQE simulation continued at a fixed temperature of 75 C to gypsum saturation. This portion of the reaction simulation in both codes is described in greater detail in the following section.

4.5.2 Results and Discussion

The initial solution compositions calculated from the input described in the preceeding section are given in Table 4-17. The first two columns of numbers in this table were calculated by EQ3 and PHREEQE using the DEQPAK7 data set. As was the case in the earlier test problems, when used with identical data sets, both codes give identical results.

The third column contains the results of PHREEQE calculations using the PREPHR data base. These results differ significantly from those achieved using the DEQPAK7 data base. To explore these differences further, the values of the equilibrium constants for the dissolution reactions of four minerals important in controlling the solution composition in this test problem are shown in Table 4-18. The minerals controlling the initial solution composition are calcite and dolomite. As this table shows the values for log $K_{calcite}$ differ by only 0.05 log units at 25 C, but the values for log $K_{dolomite}$ differ by more than a full log unit. This is reflected in the differences in the compositions calculated using the two data sets and shown in Table 4-17. The largest differences in solution composition between the DEQPAK7 and PREPHR results are in the magnesium concentration which directly reflects differences in equilibrium constant values for dolomite. Calcium, carbonate, and pH are also effected by dolomite dissolution and values for these parameters, too, differ between the two data sets, although not as much as the magnesium difference.

EQ6 and PHREEQE were used to simulate the solution of gypsum with an accompanying temperature rise in this initial solution. As gypsum goes into solution it is accompanied by the precipitation of a certain amount of calcite and the dissolution of a certain amount of

Table 4-17: Calculated Compositions of Initial Solutions for Test Problem 5 Using EQ3 with DEQPAK7 Data and Using PHREEQE with both DEQPAK7 and PREPHR Data.

CONSTITUENT	DATA SET:	DEQPAK7		PREPHR
	CODE:	EQ3	PHREEQE	
Sodium*	(log molality)	- 3.000	- 3.000	- 3.000
Calcium	(log molality)	- 2.822	- 2.822	- 2.946
Magnesium	(log molality)	- 3.845	- 3.845	- 3.017
Total Carbonate	(log molality)	- 2.442	- 2.442	- 2.346
Sulfate*	(log molality)	-10.000	-10.000	-10.000
Chloride*	(log molality)	- 3.000	- 3.000	- 3.000
pH	(units)	7.307	7.307	7.392
pe	(units)	4.000	4.000	4.000
Ionic Strength	(moles)	0.0058	0.0058	0.0071
P_{CO_2}*	(atmospheres)	0.010	0.010	0.010
Gypsum Saturation Index		- 8.336	- 8.337	- 8.493
Anhydrite Saturation Index		- 8.921	- 8.922	- 8.704
Calcite Saturation Index*		0.000	0.000	0.000
Dolomite Saturation Index*		0.000	0.000	0.000
Temperature (Celsius)*		25.0	25.0	25.0

* Values fixed by input

Table 4-18: Log K Values of Minerals Controlling Solution Composition in Test Problem 5.

Mineral	Temp. (Celsius)	log $K_{dissolution}$ DEQPAK7 Data	log $K_{dissolution}$ PREPHR Data
Calcite ($CaCO_3$)	25	- 8.525	- 8.475
	75	- 9.117	- 9.035
Dolomite ($CaMg(CO_3)_2$)	25	-18.061	-17.020
	75	-19.497	-17.893
Gypsum ($CaSO_4 \cdot 2H_2O$)	25	- 4.850	- 4.848
	75	- 4.984	- 4.820
Anhydrite ($CaSO_4$)	25	- 4.265	- 4.637
	75	- 4.954	- 5.034

Table 4-19: Calculated Mass Transfer and Solution Composition from Gypsum Dissolution and Temperature Rise from EQ6 with DEQPAK7 Data and by PHREEQE with Both DEQPAK7 and PREPHR Data.

CODE	DATA SET		Gypsum Dis-solved (mmOL)	Saturation Index Gypsum	Saturation Index Anhy-drite	Mass Transfer (mmol) Calcite	Mass Transfer (mmol) Dolo-mite	Temper-ature (Celsius)
EQ3	DEQPAK7		0.0	-8.336	-8.921	0.	0.	25.00
PHREEQE	DEQPAK7	Initial Solution	0.0	-8.337	-8.922	0.	0.	25.00
PHREEQE	PREPHR	Initial Solution	0.0	-8.493	-8.704	0.	0.	25.00
EQ6	DEQPAK7		5.000	-0.405	-0.716	- 1.024	0.284	50.00
PHREEQE	DEQPAK7		5.000	-0.405	-0.716	- 1.026	0.284	50.00
PHREEQE	PREPHR		5.000	-0.646	-0.628	- 4.300	1.931	50.00
EQ6	DEQPAK7		10.000	-0.019	-0.042	- 2.001	0.596	75.00
PHREEQE	DEQPAK7		10.000	-0.012	-0.042	- 2.003	0.597	75.00
PHREEQE	PREPHR		10.000	-0.474	-0.261	-11.200	5.614	75.00
EQ6	DEQPAK7	Gypsum	10.209	0.000	-0.030	- 2.046	0.611	76.05
PHREEQE	DEQPAK7	Saturation	10.227	0.000	-0.030	- 2.039	0.613	75.00
EQ6	DEQPAK7	Anhydrite-Gypsum Satn.	10.557	0.000	0.000	- 2.059	0.611	77.78
PHREEQE	PREPHR	Anhydrite Saturation	16.345	-0.214	0.000	-19.307	9.239	75.00

Table 4-19: (Continued).

pH	Total log molality: Ca	Mg	CO_3	SO_4
7.307	-2.822	-3.845	-2.442	-10.000
7.307	-2.822	-3.845	-2.442	-10.000
	-2.946	-3.017	-2.346	-10.000
6.716	-2.239	-3.370	-2.501	- 2.301
6.716	-2.239	-3.370	-2.501	- 2.301
6.829	-2.424	-2.539	-2.390	- 2.301
6.386	-1.996	-3.131	-2.552	- 2.000
6.386	-1.996	-3.131	-2.552	- 2.000
6.359	-2.323	-2.182	-2.426	- 2.000
6.375	-1.988	-3.122	-2.554	- 1.991
6.353	-1.987	-3.121	-2.552	- 1.990
6.363	-1.991	-3.123	-2.557	- 1.993
6.326	-2.130	-1.994	-2.434	- 1.787

dolomite. The amount of calcite and dolomite mass transfer accompanying the dissolution of varying amounts of gypsum together with the solution compositions which result at the reaction steps listed are shown in Table 4-19. As before, calculations were made using the DEQPAK7 data base with both the EQ6 and PHREEQE codes and with the PREPHR data base and the PHREEQE code. When used with the DEQPAK7 data set, both codes give essentially identical results at the points where 5 and 10 mmol of gypsum have been dissolved and show, for example, that 10 mmol of gypsum solution are accompanied by 2.0 mmol of calcite precipitation and 0.6 mmol of dolomite dissolution. At this point also, the gypsum saturation index is less than -0.02 showing that gypsum is nearly saturated.

The results of the PHREEQE simulation using the PREPHR data base to the same point of 10 mmol of gypsum solution give quite different results. As Table 4-19 shows, the simulation with this data base has 11.2 mmol of calcite precipitating and 5.6 mmol of dolomite dissolving and results in a solution with a gypsum saturation index of -0.5 far removed from gypsum saturation. The differences between the amount of calcite and dolomite mass transfer calculated using each of the two data sets are large and illustrate the fact that data set differences may give rise not only to differences in solution compositions but to differences in calculated mass transfer amounts as well.

Following reaction to the specified point of 10 mmol gypsum solution at 75 C, the EQ6 simulation continued with gypsum addition and temperature rise according to equation (4.5.3) until the solution became saturated with gypsum. As Table 4-19 shows, this required reaction progress of 10.209 mmol and reached a temperature of 76.05 C.

In the constant temperature EQ6 simulations of the previous problems, when a reactant saturated, the simulation stopped. In this problem, temperature also varies with reaction progress and is therefore a dependent variable. Thus, the simulation continued even after the reactant gypsum first saturated. The next point of interest on the reaction path occurred at 10.557 mmol of reaction progress at a temperature of 77.785 C when the solution also become saturated with the mineral anhydrite ($CaSO_4$).

The temperature at which gypsum and anhydrite are in equilibrium can be calculated manually from the equilibrium constants for the two minerals given in the DEQPAK7 data set. These calculations yield an equilibration temperature of 77.785 C. This is the same as that calculated by the EQ6 code and thus, serves to verify the correct operation of the temperature changing portions of that code.

The structure of the PHREEQE code is not such that temperature can be treated as a dependent variable and found as the result of a code operation. A solution such as the one described here if in equilibrium with both gypsum and anhydrite is constrained by the phase rule to exist only at one temperature. Thus, to PHREEQE, which accepts only arbitrary, externally set temperatures, a solution in which both anhydrite and gypsum are saturated is in apparent violation of the phase rule and cannot be treated.

For additional points of comparison among the data set and code combinations, the PHREEQE simulations were continued at an arbitrary temperature of 75 C until the first of either gypsum or anhydrite saturation occurred. As Table 4-19 shows, with the DEQPAK7 data set, gypsum saturation occurred after dissolution of 10.227 mmol, essentially the same value as calculated by EQ6 but at slightly different temperature because of the difference in the manner in which the two codes treat temperature.

With the PREPHR data set however, anhydrite first saturated after 16.345 mmol gypsum had dissolved. This is a further illustration of the very great differences in reaction path simulations which may be brought about by differences in thermodynamic data.

5 SUMMARY AND CONCLUSIONS

Geochemical processes will profoundly influence the behavior of nuclear waste repositories. Thus, models to quantitatively estimate the extent of geochemical effects on repository performance are included within the SCEPTER Package. After describing the criteria for geochemical model selection and the application of geochemical models to performance assessment, this report discusses the models selected in terms of their conceptual basis and thermodynamic data requirements. The report further describes five code comparison and verification problems which were posed and solved in order to provide code verification and to illustrate the operating features of the codes. User manuals for the codes are presented in separate reports, (INTERA, 1982a,b).

Two computer codes were selected for inclusion in the SCEPTER Package following a careful review of the literature on the state-of-the-art of geochemical modeling. The codes selected are:

- PHREEQE- (Parkhurst, Thorstenson, and Plummer, 1980) 12-Jan-1981 version, modified slightly to meet SCEPTER requirements; and
- EQ3/EQ6-(Wolery 1979) EQ3.3015U19, 9-Apr-1981 and EQ6.3015U93, 28-Mar-1981 versions.

Criteria for the selection of these codes included:

- The generality of the coded algorithms
- The non-proprietary nature of the codes and their general availability
- Their ease in portability from one computation system to another
- Their operating efficiency
- The need for one code to include the capability, at least in principle, to handle reaction rates and solid solutions.

Geochemical models will be applied in the areas of:

- Far-Field Performance Assessment -- In this area the focus is on the ground-water transport of radionuclides.

This requires knowledge of the retardation of nuclides which may result from geochemical reactions between the moving solution and the stationary aquifer framework. In most transport models, the solid- solution interaction is described by a simple linear isotherm. While this isotherm is often taken to result from the operation of sorption processes, it is in fact determined by all of the chemical reactions which may occur between fluid and solid phases and among the several solid phases themselves. Geochemical modeling in Far-Field Performance Assessment is used to simulate these reactions in order to realistically evaluate the mass partition and retardation coefficients required for transport calculations.

- Near-Field Performance Assessment - Concerns of the Near-Field include processes operating in the repository itself and influencing the behavior of the waste package. Within the repository, the same sort of transport calculations will be required as are needed for Far-Field Performance Assessment and geochemical models will be required there as well to estimate values of mass partition coefficients. Geochemical influences on the waste package are in the areas of cannister corrosion, nuclide leach rate from the waste form, and nuclide transport through the back-fill. Geochemical modeling will be required to assess the behavior of the waste package in all three areas.
- Data Acquisition Needs and Test Data Evaluation - Geochemical models when used in a sensitivity analysis mode will help set priorities and specify the precision needed in laboratory and field collection of thermodynamic data and of water and rock chemical data. Geochemical models are also needed to assist in the interpretation of data collected as part of specific site evaluations.

Widely available and generally known geochemical codes are of two types:

- Aqueous solution models which calculate thermodynamically important quantities such as free-ion activities from the measured chemical compositions of solutions. These ion activities are then used to calculate mineral saturation indices, gas partial pressures, solution oxidation states, and so forth. Well known codes of this type include SOLMNEQ and WATEQ and their derivatives, and EQ3.
- Geochemical reaction models which describe changes in the chemistry of solutions and of associated solids which occur as reactions proceed and which calculate the behavior of reacting systems in terms of the masses of elements which are transferred between solid phases and the solution or from one solid to another. Well known codes of this type include PATHI, EQ6, and PHREEQE.

The conceptual basis of the aqueous solution model included in both the PHREEQE and the EQ3/EQ6 codes is that of ion-association or ion-complexing. This assumes that oppositely charged dissolved ions react to form complexes which are in equilibrium with the free-ions as described by thermodynamic equilibrium constants. This approach has been used in aqueous geochemistry since Garrels and Thompson (1962) used it to interpret the chemistry of sea-water. It is also embodied in most widely used geochemical codes. Because of its wide use in geochemistry, thermodynamic data on many species of importance in natural waters are available for use with it.

The ion-association conceptual model becomes less capable of representing real solution behavior as the salinity of the solution increases. In general, the model performs adequately in solutions with salt contents up to a few molal, but its validity decreases rapidly in such highly saline waters as brines.

A second conceptual solution model, the mixed electrolyte model, is coming into use in geochemistry for its ability to reproduce the behavior of solutions at all concentrations. In spite of the necessity to treat brines associated with some proposed repository

environments, no mixed electrolyte model is presently included in the SCEPTER Package. This is due to the fact that not only is there no generally available code which embodies the mixed electrolyte conceptual model, but also only limited experimental data on the coefficients which must be used to employ this model.

Ion-association models such as are included in PHREEQE and EQ3/EQ6 solve two main sets of equations. These are:

- A set of mass balance equations equivalent to the number of chemical elements for which analytic data are given; and
- A set of mass action equations, one for each of the ion pair species which may result from interactions among the given elements.

The mass balance equations are written in terms of moles of the elements while the mass action equations are expressed in terms of the thermodynamic activities of the solution species. Thus, activity coeffient expressions must be available, relating the elemental activities and masses in order to solve the system. Subsidiary equations or input data may also be required depending on the problem. These may include a requirement that solution pH be input or that solution electroneutrality be included in the set of equations. Also some means of specifying solution oxidation potential is required. This could be an input oxidation potential itself or the concentration of an active redox couple or of an electro-active substance such as oxygen gas.

In PHREEQE, the set of equations so generated is solved by a continued fraction approach to successive approximations coupled with a Newton-Raphson iteration scheme. In EQ3, the equations are also solved by a successive approximation scheme controlled by a monotone sequence method. While both PHREEQE and EQ3 have all the solution modeling capabilities of, for example the WATEQ/SOLMNEQ group of codes, they have the added capability of describing quantitatively the effects of geochemical reactions. They do this by describing changes in solution composition and in relative masses of solids as a system comprising solids, gases and a solution, reacts toward a new equilibrium state following a perturbation. The description is in

terms of the masses of material transferred from phase to phase during the reaction and they are thus known as mass transfer or as reaction path modeling. PHREEQE can be considered a mass transfer model for it solves directly for the final equilibrium state of the system given a set of initial conditions. EQ6 on the other hand, employs the reaction path approach by which small steps of reaction progress are taken from an initial state toward equilibrium and the entire reaction path including the appearance and disappearance of ephemeral phases is calculated, rather than simply the mass transfer involved in the overall reaction from the initial to the final state.

Mass transfer modeling tends to be more efficient in terms of thermodynamic data needs and computer time than does reaction path modeling. Thus, it may be more frequently employed for far-field calculations where, because of the long times involved, equilibrium may be assumed. Reaction models, though, will be necessary for near-field and shorter time calculations where overall equilibrium may not be attained in the time of interest and intermediate reaction steps will be important.

To employ any geochemical model requires that thermodynamic data be available on all solution and solid species of importance in the system of interest. These data include equilibrium constants for all mass action expressions and for the dissolution of solid phases and gases of importance to the system. Information on the variation of these equilibrium constants with temperature is important. This information can be accepted in a variety of ways including the input of reaction enthalpy (ΔH) values or as values of coefficients for polynomial expressions for log K in terms of temperature.

Activity coefficient values for dissolved species and for water itself must also be known. Several expressions are available in each code to calculate these coefficients as a function of the ionic strength of the solution. These include different expressions for neutral solute species and for charged solute species.

Activity coefficients of neutral solute species are calculated in EQ3 using a polynomial expression in ionic strength which reproduces the measured activity coefficients of dissolved CO_2. In PHREEQE the activity coefficient of neutral species is taken simply as 0.1 times the ionic strength.

A number of expressions are available for calculating activity coefficients of charged solute species. All are based on the extended Debye-Huckel expression to which a term, linear in ionic strength, is added to accomodate the general increase in activity coefficients noted at ionic strengths of about 1 molar and above. A variety of options are available to choose the values of the coefficients in the extended Debye-Huckel expression in both PHREEQE and EQ3/EQ6.

Five test problems were designed and executed using both codes in order to:

- Provide code verification by means of code-to-code and code-to-hand calculation comparison; and
- To illustrate and test the various operating options available in the codes.

For code-to-code verification it was necessary that the same thermodynamic data base be available for use in each code. The two thermodynamic data sets available were:

- The DEQPAK7 set which accompanied the version of EQ3/EQ6 which was adopted; and
- A data set, here designated PREPHR, included with the published description of the PHREEQE code (Parkhurst, Thorstenson, and Plummer, 1980).

The EQ3/EQ6 package includes a code EQTL which produces a working data set for the EQ3/EQ6 codes from the DEQPAK7 data set. For code-to-code comparison purposes, EQTL was extensively modified to the code here designated PHTL which writes DEQPAK7 data in a form readable by PHREEQE. In addition, a code PQTL was written to write data from the PREPHR set in a form readable by EQ3/EQ6. Users manuals for these three data handling codes are given with the documentation of the geochemical codes themselves (INTERA, 1982a,b).

In Test Problem 1, the aqueous speciation routines in EQ3 and in PHREEQE were tested against each other and against hand calculation by applying them to the major ions dissolved in sea water. Agreement between the results of running the two codes with each other and with

hand calculations were sufficiently good to demonstrate the correct coding and solution of the algorithms.

In Test Problem 2, the aqueous speciation routines in both code were tested further by applying them to a full sea water analysis. Both PREPHR and DEQPAK7 data were used in each code. When the same data set is used, the results from each code's calculation agree within the limits of the activity coefficient expressions adopted, and served by this code-to-code comparison to verify each of the codes. Results using the two data sets in the same code, while showing reasonable agreement among the major ion species, demonstrate that differences of as much as an order of magnitude exist in the minor element data in the two data sets.

Test Problem 3 simulates the dissolution of microcline in dilute HCl. This problem tests and illustrates the reaction path modeling and phase boundary locating capabilities of the two codes in a relatively simple system which does not involve redox reactions. When run with the DEQPAK7 data set, both codes give, essentially, identical results and provide code-to-code verification of each. The same problem when run using PREPHR data and the PHREEQE code give quite different results and illustrate again the differences between the two data bases.

Test Problem 4 simulates the reduction of an oxygenated calcite- and hematite-saturated solution by the addition of methane, and was designed to demonstrate the ability of the codes to simulate reaction paths in which radical oxidation state changes occur. Both codes were run using the DEQPAK7 data. The results of both are in essential agreement and provide both code-to-code verification and an illustration of the ability of both codes to handle extreme changes in redox state during a reaction path simulation.

Test Problem 5 simulates the dedolomitization of a carbonate rock by gypsum dissolution with increasing temperature. The preceeding four problems were all at 25 C and this problem was designed to test and illustrate the ability of the codes to change temperature. Both codes were run using DEQPAK7 data and a third run was made with PHREEQE using PREPHR data. When used with the same thermodynamic

data, the results of the two codes are essentially identical and provide code-to-code verification of their ability to treat varying temperatures.

In EQ6 it is possible to associate temperature change with reaction progress so that the temperature associated with a phase boundary can be determined. In PHR81, on the other hand, temperature is always an independent variable. As in the previous examples, the results using PREPHR data differed considerably from those using DEQPAK7 data and illustrate again the differences between the two data sets.

6 REFERENCES

Ames, L.L. and Rai, Dhanpat, 1978. Radionuclide Interactions With Soil and Rock Media; Volume 1: Processes Influencing Radionuclide Mobility and Retention, U.S. Environmental Protection Agency (EPA) 520/6-78-007, 307 p.

Baes, Charles F., and Mesmer, Robert E., 1976. The Hydroloysis of Cations, New York, John Wiley and Sons, 487 p.

Ball, J.W., Jenne, E.A., and Cantrell, M.W., 1981. "WATEQ3: A Geochemical Model with Uranium Added", U.S. Geol. Survey Open File Report 81-1183, 81 p.

Ball, James W., Jenne, Everett A., and Nordstrom, D.K., 1979. "WATEQ2 - A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters", in Jenne, Everett A., ed. Chemical Modeling in Aqueous Systems: American Chemical Society Symposium Series 93, pp. 815-835.

Ball, James W., Nordstrom, D. Kirk, and Jenne, Everett A., 1980. "Additional and Revised Thermochemical Data and Computer Code for WATEQ2 -- A computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters", U.S. Geological Survey Water Resources Investigations, 78-116, 109 p.

Benson, L.V., Carnahan, C.L., and Che, M., 1980. A Study of Rock-Water-Waste Interactions in the Pasco Basin, Washington: Part II. Preliminary Equilibrium-Step Simulations of Basalt Diagenesis. Berkeley, CA., Lawrence Berkeley Laboratory, LBL-9677 2/2, 27 p.

Benson, L.B., and Teague, L.S., 1980. A Tabulation of Thermodynamic Data for Chemical Reactions Involving 58 Elements Common to Radioactive Waste Package System, Berkeley, CA., Lawrence Berkeley Laboratory, LBL-11448, 97 p.

Deutsch, William J., 1980. Geochemical Modeling of the Nuclear-Waste Repository System - A Status Report, Richland, WA., Pacific Northwest Laboratory, PNL-3518, 21 p.

Eugster, Hans P., Harvie, Charles E., and Weare, John H., 1980. "Mineral Equilibria in a Six-Component Seawater System, $Na-K-Mg-Ca-SO_4-Cl-H_2O$, at 25 C", Geochimica et Cosmochimica Acta: v. 44, pp. 1335-1347.

Garrels, Robert M. and Christ, Charles L., 1965. Solutions, Minerals and Equilibria, New York, Harper and Row, 450 p.

Garrels, R.M. and Thompson, M.E., 1962. "A Chemical Model for Sea Water at 25 C and One Atmosphere Total Pressure", American Journal of Science, v. 260, pp. 57-66.

Gevantman, L.H., ed., 1981. Physical Properties Data for Rock Salt, U.S. National Bureau of Standards Monograph 167, 288 p.

Haas, J.L., Jr., and Fisher, J.R., 1976. "Simultaneous Evaluation and Correlation of Thermodynamic Data", American Journal of Science, v. 276, pp. 525-545.

Harvie, Charles E. and Weare, John H., 1980. "The Prediction of Mineral Solubilities in Natural Waters: The $Na-K-Mg-Ca-Cl-SO_4-H_2O$ System from Zero to High Concentrations at 25 C," Geochimica et Cosmochimica Acta, v. 44, pp. 981-997.

Helgeson, Harold C., 1969. "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures", American Journal of Science, v. 267, pp. 729-804.

Helgeson, Harold C., Brown, Thomas H., and Leeper, Robert H., 1969. Handbook of Theoretical Activity Diagrams Depicting Chemical Equilibria in Geologic Systems Involving an Aqueous Phase at One Atm and 0° to 300°C, San Francisco, Freeman, Cooper and Co., 253 p.

Helgeson, Harold C., Brown, Thomas H., Nigrini, Andrew, and Jones, Thomas A., 1970. "Calculation of Mass Transfer in Geochemical Processes Involving Aqueous Solutions", Geochimica et Cosmochimica Acta, v. 34, pp.569-592.

Helgeson, Harold C., Delany, Joan M., Nesbitt, H. Wayne, and Bird, Dennis K., 1978. "Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals", Am. Jour. Science, Vol. 278-A, pp. 1-229.

Holland, Heinrich D., 1978. The Chemistry of the Atmosphere and Oceans, New York, John Wiley and Sons, 351 p.

INTERA Environmental Consultants, 1983a. PHREEQE: A Geochemical Speciation and Mass Transfer Code Suitable for Nuclear Waste Performance Assessment, ONWI-435, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH.

INTERA Environmental Consultants, 1983b. EQ3/EQ6: A Geochemical Speciation and Reaction Path Code Package Suitable for Nuclear Waste Performance Assessment, ONWI-472, prepared for Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH.

Jenne, Everett A., 1981. Waste/Rock Technology Program Geochemical Modeling: A Review, Richland, WA., Pacific Northwest Laboratory, PNL-3514, 47 p.

Kharaka, Y.K., and Barnes, I., 1973. SOLMNEQ: Solution-Mineral Equilibrium Computations, U.S. Dept. of Commerce, National Technical Information Service PB215-899, 88 p.

Kielland, Jacob, 1937. "Individual Activity Coefficients of Ions in Aqueous Solutions", American Chemical Society Journal, v. 59, pp. 1675-1678.

Lewis, Gilbert N., and Randall Merle, 1961. Thermodynamics, Second edition, Revised by Pitzer, Kenneth S., and Brewer, Leo: New York, McGraw-Hill, 723 p.

Mercer, J.W., Faust, C.R., Miller, W.J., and Pearson, F.J., Jr., 1981. "Review of Simulation Techniques for Aquifer Thermal Energy Storage (ATES), in: Advances in Hydroscience: Vol. 13, Academic Press, Inc., New York, pp. 1-129.

Moody, Judith B., 1982. Radionuclide Migration/Retardation: Research and Development Technology Status Report, Columbus, OH., Office of Nuclear Waste Isolation, Battelle Memorial Institute, ONWI-321, 61 p.

Morel, Francois, and Morgan, James, 1972. "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems", Environmental Science and Technology, v. 6, pp. 58-67.

Nordstrom, D.K., Plummer, L.N., Wigley, T.N.L., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.N., Fritz, B., Hoffman, M., Holdren, G.R., Jr., Lafon, G.N., Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.F., Sposito, G., and Thrailkill, J., 1979. "A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems", in Jenne, E.A., ed.: Chemical Modeling in Aqueous Systems: American Chemical Society Symposium Series 93, pp. 857-892.

Parkhurst, David L., Thorstenson, Donald C., and Plummer, L. Niel, 1980. PHREEQE - A Computer Program for Geochemical Calculations, U.S. Geological Survey Water-Resources Investigations 80-96, 210 p.

Pearson, F.J., Jr., 1981. Geochemical Aspects of Nuclear Waste Transport Modeling, Geological Society of America Abstracts with Programs, v. 13, No. 7, p. 527.

Peiper, J. Christopher, and Pitzer, Kenneth S., 1981. Thermodynamics of Aqueous Carbonate Solutions Including Mixtures of Sodium Carbonate, Bicarbonate and Chloride, Berkeley, CA., Lawrence Berkeley Laboratory LBL-12725, 44 p. [preprint of manuscript submitted to Journal of Chemical Thermodynamics].

Pitzer, Kenneth S., 1973. "Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations", Journal of Physical Chemistry, v. 77, pp. 268-277.

Pitzer Kenneth S. and Kim, Janice J., 1974. "Thermodynamics of Electrolytes: IV. Activity and Osmotic Coefficients For Mixed Electrolytes", Journal Am. Chem. Soc., v. 96, pp. 5701-5707.

Plummer, L. Niel, Jones, Blair F., and Truesdell, Alfred H., 1976. WATEQF - A Fortran IV Version of WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters, U.S. Geological Survey Water-Resources Investigations 76-13, 63 p. [Revised and Reprinted, December 1978].

Plummer, L.N., Parkhurst, D.L. and Kosiur, D.R., 1975. MIX2: A Computer Program for Modeling Chemical Reactions in Natural Waters, U.S. Geological Survey Water-Resources Investigations 75-61, 68 p.

Rai, Dhanpat, and Serne, R.J., 1978. Solid Phases and Solution Species of Different Elements in Geologic Environments, Richland, WA., Pacific Northwest Laboratory, PNL-2651, 129 p.

Reilly, P.J., Wood, R.H., and Robinson, R.A., 1971. "The Prediction of Osmotic and Activity Coefficients in Mixed-Electrolyte Solutions", Journal of Physical Chemistry, v. 75, pp. 1305-1315.

Robie, Richard A., Hemingway, Bruce S. and Fisher, James R., 1978. Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures, U.S. Geological Survey Bulletin 1452, 456 p., [Reprinted with corrections, 1979].

Robinson, Gilpin, R., Jr., Schafer, Constance M., and Haas, John L., Jr., 1981. Feasibility Study of Data for Nuclear-Waste Disposal -- Thermodynamic Properties of Basalt, Granite, Shale and Tuff, U.S. Geological Survey Open-File Report 81-470, 134 p.

Robinson, R.A. and Stokes, R.H., 1970. Electrolyte Solutions, Second edition (Revised): London, Butterworths, 571 p.

Smith, M.J. principal author, 1980. Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge, Richland, WA., Rockwell Hanford Operations RHO-BWI-ST-7, 617 p.

Stumm, Werner and Morgan, James J., 1981. Aquatic Chemistry, 2nd ed.: New York, John Wiley and Sons, 780 p.

Thorstenson, Donald C., Fisher, Donald W., and Croft, Mack G., 1979. The Geochemistry of the Fox Hills-Basal Hill Creek Aquifer in Southwestern North Dakota and Northwestern South Dakota, Water Resources Research, v. 15, pp. 1479-1498.

Truesdell, A.H.,and Jones, B.J., 1973. WATEQ: A Computer Program for Calculating Chemical Equilibria of Natural Waters, National Technical Information Service PB2-20464, 77 p.

Truesdell, Alfred H., and Jones, Blair, F., 1974. WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters, U.S. Geological Survey Journal of Research, v. 2, pp. 233-248.

Vieth, J.A., and Sposito, Garrison, 1977. "On the Use of the Langmuir Equation in the Interpretation of "Adsorption" Phenomena", Soil Science Society of America Journal v. 41, pp. 697-702.

Wigley, T.M.L., 1977. WATSPEC: A Computer Program for Determining the Equilibrium Speciation of Aqueous Solutions, British Geomorphological Research Group Technical Bulletin, v. 20, 48 p.

Wolery, T.J., 1979. Calculation of Chemical Equilibrium Between Aqueous Solution and Minerals: The EQE/6 Software Package, Livermore, CA., Lawrence Livermore Laboratory, UCRL-52658, 41 p.

Wolery, T.J., 1980. Chemical Modeling of Geologic Disposal of Nuclear Waste: Progress Report and a Perspective, Livermore, CA., Lawrence Livermore Laboratory, UCRL-52748, 66 p.

Wolery, Thomas J., and Walters, Lester J.Jr., 1975. Calculation of Equilibrium Distributions of Chemical Species in Aqueous Solutions by Means of Monotone Sequences, Mathematical Geology, v. 7, pp. 99-115.

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