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PHREEQE—A COMPUTER PROGRAM FOR GEOCHEMICAL CALCULATIONS

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 80-96

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By David L. Parkhurst, Donald C. Thorstenson, and L. Niel Plummer

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PREFACE

This revision marks several changes to the PHREEQE Source Code and Data Base. The current version is written in Fortran 77 and runs on a Prime, Inc. Model 850 minicomputer. Attachment B lists the current Fortran 77 Source Code. The convergence criteria used in the Newton-Raphson iteration scheme have been improved. Convergence is still not assured, but fewer problems have been encountered in testing. A new keyword, KNOBS, has been added which gives the user capability to adjust the convergence criteria. KNOBS input is described under "Description of Input". A new unit of input concentration, mmol/kg of solution, is now accepted (IUNITS=4). The form of the analytical expression for Log K under MINERALS and LOOK MIN input has been changed to

$$\log K = A + BT + C/T + D \log T + E/T^2$$

and corresponding changes to the data base have been made.

Attachment A lists the current PHREEQE data base. Changes have been made to the equilibrium constant expressions for calcite, aragonite, strontianite, celestite, gypsum, anhydrite, siderite, and barite. Aqueous species affected include $CaHCO_3^+$, $CaCO_3^\circ$, $CO_2(aq)$, HCO_3^-, CO_3^{2-}, $SrHCO_3^+$, $SrCO_3^\circ$, and $SrSO_4^\circ$. Most of these revisions reflect two recent publications (Plummer and Busenberg, 1982; and Busenberg, Plummer, and Parker, 1984). But, in general, the data base remains little changed. undocumented and should not be used without careful checking. A companion program to PHREEQE (PHRQINPT) is now available for interactive construction of PHREEQE input data sets (Fleming and Plummer, 1983).

With this revision, only Test Problem 1 has been updated to the current version and data base. The test results of Test Problems 2-5 given in the section "Test Problems" have not been updated. Because of the changes mentioned above, similar, but not identical, results can be expected for Test Problems 2-5.

Plummer, L.N., and Busenberg, E., 1982, The solubilities of calcite, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O: Geochimica et Cosmochimica Acta, v. 46, p. 1011-1040.

Fleming, G.W., and Plummer, L.N., 1983, PHRQINPT - An interactive computer program for constructing input data sets to the geochemical simulation program PHREEQE: U.S. Geological Survey Water-Resources Investigations Report 83-4236, 108 p.

Busenberg, E., Plummer, L.N., and Parker, V.B., 1984, The solubility of strontianite ($SrCO_3$) in CO_2-H_2O solutions between 2 and 91°C, the association constants of $SrHCO_3^+$(aq) and $SrCO_3^\circ$(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr^{2+}(aq) and $SrCO_3$(cr) at 25°C and 1 atm total pressure: Geochimica et Cosmochimica Acta, v. 48, p. 2021-2035.

DLP, DCT, LNP
January 14, 1985

PREFACE FOR AUGUST 1990 REVISION

A new data base is included with this revision of PHREEQE. The data listed in Attachment A are consistent with the data published by Nordstrom and others, 1990. The new listing of source code is found in Attachment B. Only minor revisions have been made to the numerical method of the program. However, changes have been made (1) to streamline the linear equation solver, (2) to enable the aqueous model to be enlarged, and (3) to simplify the definition of file unit numbers.

The linear equation solver, subroutine SLNQ, has been streamlined to perform only Gaussian elimination (eliminating the determinant option that was not used) and to increase execution speed.

Changes have been made in the source code to facilitate the use of PHREEQE for problems that require larger numbers of elements and (or) species than were previously allowed. The sizes of the data arrays for ELEMENTS, SPECIES, LOOK MIN, MINERALS, and SUMS are now set at compile time by one Fortran PARAMETER statement located in the COMMON.BLOCKS file. The following parameters define the sizes of arrays:

MAXT - the maximum number of ELEMENTS and master species. Default is 30.
MAXS - the maximum number of aqueous SPECIES. Default is 250.
MAXM - the maximum number of MINERALS. Default is 20.
MAXLK - the maximum number of LOOK MIN minerals. Default is 200.
MAXSUM - the maximum number of SUMS. Default is 10.
MXINSM - the maximum number of species that can be included in any one of the SUMS. Default is 50.

The default sizes are the same as previous versions of PHREEQE except that the number of LOOK MIN minerals has been increased from 40 to 200. Enlarging the array sizes should cause no problems with the execution of the program, except for the case of MAXT. Enlarging MAXT has important consequences to the rest of the data base. The current data base begins numbering complexes (non-master species) at 31 (that is, greater than the default MAXT of 30). If MAXT is made larger, then the numbering of complexes must be changed so that all numbers of complexes are greater than the new MAXT. A further consequence is that some MINERAL and LOOK MIN minerals can contain complexes in their dissociation reactions. Care must be taken to ensure that any changes to the numbering of complexes are also applied to mineral formulas.

Another change to the source code was made to facilitate the handling of file unit numbers by PC's and other computers. The three files needed to run PHREEQE are the input file, the output file, and the data base. The Fortran unit numbers for these files are now defined in one Fortran PARAMETER statement in the COMMON.BLOCKS file. The parameter names and the default settings are: IR = 5, input file; IW = 6, output file; and IDB = 11, data base. The default settings are the same as previous versions of PHREEQE. The three files are not opened within the Fortran code. Either, (1) the files can be opened externally to the program at the computer operating system level before execution (this provides the greatest flexibility for changing the file names) or (2) the Fortran code can be modified to include OPEN statements. The file names could be 'hard coded' in OPEN statements (changing file names would require recompilation) or an interactive section of code could be written to solicit the names of the files, which are then opened with OPEN statements.

An interactive program, PHRQINPT, has been published that creates an input file for PHREEQE (Fleming and Plummer, 1983). This program solicits and formats the data necessary to run PHREEQE. Help is available at each prompt to explain the type of data being requested and the program contains error checking to ensure that all necessary data are included.

A separate version of PHREEQE, named PHRQPITZ, has been written and published (Plummer and others, 1988). This version uses a specific ion interaction approach to calculate activity coefficients (Pitzer, 1979 among others). PHRQPITZ is designed to provide more reliable geochemical calculations for brines. The current state of the specific ion interaction approach does not allow calculations involving redox and there are no interaction parameters for aluminum or silicon. Plummer and others (1988) describe the theoretical basis, review the literature values for interaction parameters, provide directions for the use of the program, present several sample problems, and describe the use of an interactive input program (PITZINPT).

Machine-readable copies of all of the PHREEQE family of programs (including PC versions) along with copies of the reports describing the programs are available from the National Water Information System of the Office for Scientific Information Management of the Water Resources Division:

National Water Information System
U.S. Geological Survey
437 National Center
Reston, VA 22092
(703) 648-5686

Fleming, G.W. and Plummer, L.N., 1983, PHRQINPT--an interactive computer program for constructing input data sets to the geochemical simulation program PHREEQE: U.S. Geological Survey Water-Resources Investigations Report 83-4236, 108 p.

Nordstrom, D.K., Plummer, L.N., Langmuir, Donald, Busenberg, Eurybiades, May, H.M., Jones, B.F., and Parkhurst, D.L., 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitations, *in* Bassett, R.L. and Melchior, D. eds., Chemical modeling in aqueous systems II: Washington D.C., American Chemical Society Symposium Series 416, p. 398-413.

Pitzer, K.S., 1979, Theory: Ion interaction approach, *in* R.M. Pytkowicz, (ed.), Activity Coefficients in Electrolyte Solutions, v. 1: Boca Raton, Florida, CRC Press, Inc., p. 157-208.

Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines: U.S. Geological Survey Water-Resources Investigations Report 88-4153, 310 p.

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PHREEQE - A COMPUTER PROGRAM FOR GEOCHEMICAL CALCULATIONS

David L. Parkhurst, Donald C. Thorstenson, and L. Niel Plummer

ABSTRACT

PHREEQE is a Fortran IV computer program designed to model geochemical reactions. Based on an ion pairing aqueous model, PHREEQE can calculate pH, redox potential, and mass transfer as a function of reaction progress. The composition of solutions in equilibrium with multiple phases can be calculated. The aqueous model, including elements, aqueous species, and mineral phases, is exterior to the computer code and is completely user definable. This report (1) explains the theory and equations on which the program is based, (2) describes the card input necessary to run the program, (3) contains five test cases and their results, and (4) provides listings of the computer code and the preliminary data base.

INTRODUCTION

This paper presents the latest in a series of computer programs developed by U.S. Geological Survey personnel to deal with problems that occur in surface and ground-water hydrogeochemical studies. Our purpose is to present the code for the program PHREEQE [1/] and a sufficient theoretical discussion (on an elementary level) to provide the user with a grasp of the basic chemical and thermodynamic concepts and assumptions used in PHREEQE. We will not treat in any detail the general subject of chemical modeling, as several recent and comprehensive reviews on the subject are available (Leggett, 1977; Perrin, 1977; Nordstrom and others, 1979).

Earlier Geological Survey computer programs for dealing with natural water chemistry have, in a sense, been outgrowths of the Garrels-Thompson ion-association model for seawater (Garrels and Thompson, 1962). These programs, which include WATEQ (Truesdell and Jones, 1974), SOLMNEQ

[1/] pH-redox-equilibrium-equations

(Kharaka and Barnes, 1973), WATEQF (Plummer and others, 1976), and WATEQ2 (Ball and others, 1979), are designed to calculate solution speciation and saturation states of the aqueous phase with respect to various mineral phases, given analytical concentrations of the elements, pH, temperature, and pe (if redox reactions are considered). A somewhat more sophisticated program, MIX2, does not require pH as an input variable, and can simulate heterogeneous reactions (excluding redox) and mixing of waters while following equilibrium with a single phase (Plummer and others, 1975). (Only Geological Survey programs are listed; see the aforementioned references for a general survey of the literature.)

The computer program PHREEQE is one of a smaller family of programs that are capable of following one or more phase boundaries, and calculating pH and pe (as well as mass transfer and aqueous phase speciation) as dependent variables in the calculations. In the geochemical literature, these programs have largely been outgrowths of the work of Garrels and Mackenzie (1967) and the theory and computer programs developed by Helgeson and coworkers (Helgeson, 1968; Helgeson and others, 1969; Helgeson and others, 1970).

PHREEQE can simulate several types of reactions including (1) addition of reactants to a solution, (2) mixing of two waters, and (3) titrating one solution with another. In each of these cases PHREEQE can simultaneously maintain the reacting solution at equilibrium with multiple phase boundaries. The program calculates the following quantities during the reaction simulation:

1. The pH.
2. The pe.
3. The total concentration of elements.
4. The amounts of minerals (or other phases) transferred into or out of the aqueous phase.
5. The distribution of aqueous species.
6. The saturation state of the aqueous phase with respect to specified mineral phases.

In addition, the aqueous model is completely user definable with respect to the elements and aqueous species included in the data base.

In the following sections we set out the conceptual framework of PHREEQE and present some examples. In some cases we make simplifying assumptions for purposes of comparison or discussion. Our purpose is to try to present the basic concepts in PHREEQE with a minimum of formal mathematics. For those who find this approach unsatisfactory, we refer to the original works of Helgeson and coworkers, Wolery and Walters (1975), or Wolery (1979).

As discussed by Nordstrom and others (1979), a distinction should be made between the "aqueous model", and the computer program that executes the calculations based on the model. PHREEQE uses an ion-association model that is based on the current aqueous models used in the USGS programs WATEQ, SOLMNEQ, WATEQF, and WATEQ2. Although PHREEQE is linked to the general approach of an ion-association model, the program allows the aqueous model to be user defined through choice of input data.

Recent emphasis is being placed on new models for mixed electrolyte solutions which, although semiempirical, are based on an equally sound thermodynamic foundation (Reilly and others, 1971; Pitzer, 1973; Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974; Pitzer, 1975; Wood, 1975). Recent calculations (Harvie and Weare, 1980) show that some of these models are more successful than the current ion association model used in PHREEQE in highly concentrated solutions (brines).

EQUILIBRIUM EQUATIONS

We discuss first the basic mathematical concepts used in PHREEQE. Because the aqueous model in PHREEQE is an extension of earlier work, it will be only briefly summarized in this paper. For purposes of discussing the calculation philosophy of PHREEQE, we will initially ignore the difference between the thermodynamic activity, a_i, and concentration (molality), m_i, of species in aqueous solution, and, for now, refer to [i] as the concentration/activity of species i. Although arbitrary, this introduces no conceptual problem since for every species i, activity and concentration, m_i, are related by $a_i = \gamma_i m_i$, where the activity coefficient, γ_i, can be defined for every species i. The arguments presented below are valid for any reaction path simulation program.

We begin our discussion with an analysis of a calculation for a solution that does not involve redox equilibria. The information that is needed to perform a calculation (this can represent the initial solution composition, or a calculation at any specific point along a reaction path) is the following:

Total Masses of Each Element in the System

These may represent analytical concentrations, real or assumed, in a natural water, or in the case of reaction paths, a new total concentration dictated by a specified reaction being modeled. Whatever the source, the total concentrations of the elements must be known for PHREEQE to begin any given calculation at a reaction increment. The total concentration of an element in the computer program must satisfy mass balance. For example, mass balance on calcium is written

$$\mathrm{CATOT} = \sum_i [\mathrm{Ca}_i]$$

where CATOT is the total molality of calcium and $\sum_i [\mathrm{Ca}_i]$ is the sum of the molalities of all the calcium-bearing species in solution. (Terms to include the calcium derived from mineral phases may also be present in the mass balance equation, as described in Phase Equilibria below.) Similar conservation relations are written for all the elements considered in the calculations, except H and O.

It is difficult to formulate a conservation equation for either H or O because of the contribution of H_2O. In PHREEQE we have substituted two other equations, electrical neutrality and conservation of electrons, for these two mass balance relations (see below).

Mass Action Equations for Ion Pairs

Except for the free ions (and mineral terms), all other terms appearing in the mass balance equations for the elements are ion pairs formed by the association of individual cations (X) and anions (Y). Thus, a second and obvious set of data required by PHREEQE are the equilibrium constants, K, for all the association reactions of the form

$$xX + yY = X_xY_y$$

(ignoring ion charge for simplicity) where K is given by the mass action equation,

$$K = \frac{[\ X_xY_y\ ]}{[\ X\ ]^x\ [\ Y\ ]^y} \quad .$$

The equilibrium constants are defined as a function of temperature, K(T), either through specific empirical expressions or from the enthalpy of reaction and the Van't Hoff equation.

The algebraic solution of a series of equations requires one independent equation for each algebraic unknown. In the calculation problem as we have presented it to this point, this criteria holds. That is, for each element, i, considered, we have one mass balance equation for one unknown concentration of the free species of each element and one mass action equation for each unknown concentration of an ion pair.

This equality of equations and unknowns holds because we have not yet considered H^+ and OH^-, which are not included in the above mass balance equations. Thus we have two extra unknowns, $[H^+]$ and $[OH^-]$, and one additional equation,

$$K_{H_2O} = [H^+][OH^-]$$

(taking the activity of water to be unity for now), which leaves one additional unknown, $[H^+]$ by arbitrary choice.

It is the treatment of this final variable that determines the basic nature of the computer program in question. In WATEQ and its derivative programs, pH is known analytically, input into the program, and the aqueous speciation and degree of saturation of the aqueous phase with respect to various mineral phases is calculated. In PHREEQE, an additional equation is provided and pH can be calculated as a dependent variable.

Electrical Neutrality

If pH is not input from analytical data, but is to be calculated, another equation is required. This equation for calculating pH can be derived from either mass balance (on O or H) or the electrical neutrality constraint, and provides the capability for "path-following" programs. PHREEQE uses the latter in calculation, that is, the pH of the solution is adjusted until electrical neutrality is achieved within arbitrary limits. Note that it is usually the effect of pH changes on other aqueous species that adjusts the electrical balance rather than the molality of hydronium ion itself. (Other methods of defining electrical neutrality are discussed in the description of input.)

Phase Equilibria

We can now raise the question of phase equilibria (still ignoring the question of redox reactions), and we find that conceptually, the consideration of a mineral phase adds one algebraic unknown, MIN_p, which is the quantity of the p^{th} mineral phase precipitated or dissolved in a given calculation. This term will appear in the mass balance equations for each element in the solid phase (except H and O). For example, MIN_{CaCO3} will appear as a term in both the carbon and calcium mass

balance equations. The additional equation required for each mineral added to the system is provided by the solubility product constant for the mineral (or a hydrolysis constant, or any other algebraically independent equilibrium constant) relating the mineral to the solution via a mass action equation. So for each additional mineral, we have an additional equation, and conceptually at least, the equations can be solved. Thus, in PHREEQE, regardless of the number of phases considered (provided the Gibbs phase rule is not violated), pH is ultimately specified by electrical neutrality. The available options for dealing with chemical analyses that do not perfectly balance electrically will be discussed later.

At this point we can conceptually specify an initial solution composition (from analytical data), calculate an initial pH, and equilibrate the solution with whatever phases we choose. Then, as a function of reaction or changing conditions, changes in solution chemistry are calculated. Unlike PATHI (Helgeson and coworkers) and related programs which adjust the phases and the number of phases automatically, PHREEQE requires the user to choose the exact phases present during the reaction. (See test case 5 for use of PHREEQE in path finding problems.)

Conservation of Electrons

At this point we need to consider redox reactions, and the basic differences between the role of H^+ and e^- in solution chemistry. Protons, or hydronium ions, H_3O^+, occur as physical entities present in measurable quantities in aqueous solutions. Electrons, on the other hand, although their transfer is the basis for the definition of redox reactions, occur in vanishingly small quantities under natural conditions. From a mathematical point of view, the differences/similarities between H^+ and e^- are that while the activities of either or both appear in the equilibrium constant (mass action) equations defining activity ratios or products of aqueous species, the H^+ ion appears in the electrical neutrality equation whereas $e^-_{(aq)}$ does not because it does not occur in measurable concentrations.

The introduction of pe ($-\log_{10}(a_{e^-})$) as a final algebraic unknown in the set of variables requires one additional independent equation. Again there are alternate sources for this final equation: it may be obtained by coupling mass balance on O and H in the system with electrical neutrality, or as in PHREEQE, from the fact that electrons must be conserved in the system. By the latter statement, we simply mean that although electrons do not appear (mathematically or physically) in the aqueous phase, they cannot be created or destroyed in reactions. For every molecule/ion that loses an electron through oxidation, some other molecule/ion must gain an electron. An alternative statement of this concept is that as long as electrons are neither added to nor removed from the system, the net valence state of the system must remain constant. This is basically the concept that PHREEQE uses in its bookkeeping for electrons. For example, a system composed of 1 mole of Na_2SO_4 and 1 mole of CH_4 would have a net valence state (excluding any H_2 or O_2 that might be present) of 1 x 6 (for S^{6+}) + 1 x (-4) (for C^{4-}) = +2. (Na^+ is not considered since in natural environments its valence does not change and oxygen at a valence of -2 is not considered by convention; see below). If sulfate reduction now occurs in this system, and we end up with 1 mole of Na_2S, 1 mole of CO_2, and 2 moles of H_2O, we now have 1 x (+4) (for C^{4+}) + 1 x (-2) (for S^{2-}) = +2, and we see that the valence state of the system is unchanged. For bookkeeping convenience in redox calculations PHREEQE keeps account only of those species whose valence can change over the range of pe-pH conditions covered by the chemical stability of water. Also for convenience, PHREEQE monitors only changes in concentration of dissolved O_2 and H_2 (not total masses of O and H), calculated from pH, pe, and equilibrium with H_2O. At this point we introduce the term operational valence (OPV or sometimes the THOR) and define it for each aqueous species. The OPV is defined to be the valence of any species which can change valence (can be oxidized or reduced) under naturally occurring conditions. The OPV of species which do not change valence under natural conditions is defined to be 0. The OPV of O^{-2} (oxygen with valence of -2) is 0 and the OPV of H^+ is also 0. This convention allows the masses of H_2O, H^+, and OH^- to be ignored in calculations while preserving the relative changes in valence between H^+ (0 by our convention) and H_2 (-2 by our convention) and O^{2-} (0) to O_2 (+4). The OPV state of a solution is the sum over all species of the molality of the species times its OPV.

Finally, there is one fundamental difference that must be mentioned between electrons and protons that has considerable significance for the practical question of how the calculations are set up, i.e. the actual running of the computer program. The potential problem lies in how the composition of the initial solution is specified. Total concentrations of cations and anions allow calculation of pH through the physical requirement that the solution in total must be electrically neutral. That is, with good chemical analyses (with or without the assumption of mineral equilibria) the pH can be specified, that is, it can be calculated by the computer program. This conceptually requires only the total molalities of the elements, the physical requirement of electrical neutrality, and definition of the aqueous model.

However, since the electron balance equation used by PHREEQE is written in terms of changes in concentration, it requires a reaction increment to occur before it can be used. The equation has no bearing on the initial solution specified for the system. In other words, the redox conditions in the initial solution must be specified before calculations begin. Note, for example, that if an initial solution at equilibrium with pyrite and hematite is desired, the redox characteristics of the solution prior to equilibration with the minerals must still be specified before the pe and pH of the desired solution can be calculated.

Comment

It is convenient to associate the equations and unknowns as follows: With each activity of free (uncomplexed) ion, a mass balance equation may be associated; with each ion pair, a mass action equation is associated; with each phase (other than the aqueous) a mass action equation can be associated; $[OH^-]$ is "determined" by K_{H_2O}; pH is "determined" by electrical neutrality; and pe is "determined" by conservation of electrons.

We now enter the real world and consider the fact that the thermodynamic activity and concentration are not, in general, equal. In fact, for each aqueous species we need to determine both the concentration (as molality) and activity. Thus we need one more equation for each aqueous species. The additional equations are provided by the activity-concentration relations for each species: $a_i = \gamma_i m_i$, where

a_i = thermodynamic activity

γ_i = activity coefficient

m_i = molality.

Additional computational difficulties are provided by the fact that the mass balance, charge balance, and electron balance equations sum molalities, while the mass action equations require thermodynamic activities.

Equations

In this section we formally list the equations used in PHREEQE. To facilitate this discussion, we need to introduce the concept of the "<u>master species</u>" as they are used in the computational sequence. For each element in the (computational) system, there may exist a number of aqueous species. For computational purposes, one species containing a given element must be chosen and used exclusively in writing all mass action equations for species that contain the element in question. For example, Ca^{2+} and CO_3^{2-}, the master species chosen in our example data base (Attachment A) for Ca and C, respectively, would be used to write the mass action equations for the formation of species such as $CaHCO_3^+$ $CaCO_3^o$, $Ca(OH)^+$, HCO_3^-, CH_4, $CaCO_{3(s)}$, and $CO_{2(g)}$. As a more complete example, consider the formation of S^{2-} from SO_4^{2-}. Sulfate ion is the arbitrarily chosen master species for the element sulfur. The reaction is

$$SO_4^{2-} + 8e^- + 8H^+ = S^{2-} + 4H_2O \ .$$

For the species S^{2-} the coefficients and association constant for this reaction must be entered in the data base. Each species is assigned an index number and the lowest numbers are used for master species. H^+, e^-, and H_2O are master species with index numbers 1, 2, and 3 respectively, and all other master species must have index numbers between 4 and 30, inclusive. Only master species may appear in the association reactions for aqueous ion pairs.

The equations used by PHREEQE are as follows:

1. Electrical neutrality (one equation).

$$\sum_{i=1}^{I} z_i \cdot m_i = 0$$

2. Conservation of electrons (one equation). The sum of the OPV of aqueous species equals initial total plus contribution from phases other than aqueous. This equation is only used in determining the speciation in reaction solutions, not initial solutions.

$$\sum_{i=1}^{I} v_i \cdot m_i = OPV + \sum_{p=1}^{P} u_p \cdot MIN_p$$

3. Mass balance (one equation for each element except H and O). The sum of aqueous species equals initial total plus contribution from phases other than aqueous.

$$\sum_{i=1}^{I} c_{i,j} \cdot m_i = TOT_j + \sum_{p=1}^{P} b_{p,j} \cdot MIN_p \qquad \text{for each } j$$

4. Mineral equilibrium (one equation for each mineral phase).

$$\sum_{j=1}^{J} b_{p,j} \cdot \log(a_j) = \log(K_p) \qquad \text{for each } p$$

5. Mass action equations for aqueous species (one for each aqueous species other than master species; written as association reactions).

$$\log(a_i) = \log(K_i) + \sum_{j=1}^{J} c_{i,j} \cdot \log(a_j)$$

where,

a_i	activity of the i^{th} ion-pair.
a_j	activity of the j^{th} master species.
$b_{p,j}$	stoichiometric coefficient of the j^{th} master species in the p^{th} mineral (zero if master species is not present in mass action equation for p^{th} mineral).
$c_{i,j}$	stoichiometric coefficient of the j^{th} master species in the i^{th} aqueous species (zero if master species is not present in mass action equation for the i^{th} species).
I	number of aqueous species.
J	number of master species.
K_i	equilibrium constant for the mass action equation for the i^{th} aqueous species.
K_p	equilibrium constant for the mass action equation for the p^{th} phase.
m_i	molality of the i^{th} aqueous species.
MIN_p	moles of the p^{th} mineral transferred into (+) or out of (-) the aqueous phase.
OPV	$\sum_{i=1}^{I} v_i \cdot m_i$, calculated from the speciation of the initial solution or the mixture of two initial solutions.
P	number of mineral phases.
TOT_j	Total concentration of the element corresponding to the j^{th} master species preceding any mineral dissolution or precipitation.
u_p	sum of the OPV's of the constituents in the p^{th} mineral. Ex. $u_{FeS_2} = 0$ and $u_{Fe(OH)_3} = +3$.

v_i Operational valence (OPV) of the i^{th} aqueous species. The numerical values are assigned arbitrarily for bookkeeping convenience; they are self-consistent in terms of correctly defining electron transfer in redox reactions, but may or may not correspond to the true chemical valence for the entities involved.

v_i = 0 for "non-redox" species (those whose valence does not change within the stability range for water).

= 0 for H^+,

= 0 for OH^-,

= -2 for $H_{2(aq)}$,

= +4 for $O_{2(aq)}$,

= the formal elemental valence for aqueous redox species (or the sum of the formal valences of the constituents of an aqueous complex, excluding H and O). Ex. v_{Fe2+} = +2, $v_{SO_4^{2-}}$ = +6, and $v_{FeSO_4^o}$ = +8.

z_i charge on the i^{th} species.

NUMERICAL METHOD

PHREEQE solves a set of non-linear equations using a combination of two techniques: (1) a continued fraction approach, as in Wigley (1977), is used for mass balance equations, and (2) a modified Newton-Raphson technique is used for all other equations. The independent unknowns are:

1. a_{H^+}
2. a_{e^-}
3. The activity of one aqueous species for each element, called the master species. (The master species of an element is usually chosen to be the free ion of that element, such as Ca^{2+} for calcium. All other aqueous species must have only master species in their association reactions.)
4. the amounts of mineral mass transfer to the aqueous phase.

All other unknowns, activities of other aqueous species, activity coefficients, molalities, and the activity of water are calculated from these independent variables. The activities of aqueous species are calculated from their mass action equations, which involve only master species and an equilibrium constant. Activity coefficients are calculated from either the Debye-Hückel or Davies formulation. The activity of water is calculated as in WATEQ (Truesdell and Jones, 1974).

The equations which correspond to this reduced set of variables are:

1. Electrical neutrality
2. Electron balance
3. Mass balance (one for each element other than H and O)
4. Mineral mass action equations (one for each mineral).

PHREEQE solves a set of algebraic equations using iterative techniques to approximate the solution to the equations. Unlike PATHI (Helgeson and others, 1970), the estimates at each iteration need not be exact but only good enough to ensure that the sequence of estimates converges on the algebraic solution. Thus it is possible to make the crude approximations of (1) constant activity coefficients and (2) no interdependence of species when changing activities of several master species simultaneously, at any one iteration without loss of accuracy in the final solution.

The two techniques used by PHREEQE differ fundamentally in that the continued fraction approach calculates new estimates for the master species directly while the Newton-Raphson approach actually calculates changes in a_{H^+}, a_{e^-}, and mineral transfer which, when added to the old estimates, gives the new estimate.

In the numerical scheme, there are two possibilities for each iteration. The master species are adjusted using the continued fraction method and then (1) if the mass balance equations are not satisfied within at least 20 percent, a new iteration is begun, or 2) if the mass balance are satisfied the Newton-Raphson matrix is solved and new a_{H^+}, a_{e^-}, and mineral transfer estimates are made. The pH, pe, and minerals may be held constant for several iterations (especially in the initial iterations) and are changed only when the mass balance criteria are nearly satisfied.

The following method is used to refine the estimates of the activities of the master species. It assumes that the molality of each species of an element is proportional to the activity of the master species of that element. This implies that activity coefficients are constant and the activities of other master species are constant. For element j the formula is:

$$a_{j(N+1)} = \left[a_j \cdot \frac{\mathrm{TOTAL}_j}{\sum_{i=1}^{I} m_j \cdot c_{i,j}} \right]_{(N)}$$

N indicates that all molalities, activities, and totals are those calculated at the Nth iteration. $\mathrm{Total}_{j(N)}$ is calculated from the initial total plus the sum of all the mineral transfers from all the previous iterations; other notations are the same as in the previous list of equations.

There is an oscillatory effect if this technique is applied to all master species simultaneously. However, by first correcting the positively charged master species, then redistributing all the species, and finally reestimating the negatively charged master species the effect is minimized. If a large fraction of the jth element is tied up in species in which $c_{i,j} > 1$, then a quadratic formula is used,

$$a_{j(N+1)} = a_{j(N)} \cdot \left[\frac{- B_j + \sqrt{B_j \cdot B_j + 4 \cdot A_j \cdot \mathrm{TOTAL}_j}}{2 \cdot A_j} \right]_{(N)}$$

where,

$$A_j = \sum_{i=1}^{I} m_i \cdot c_{i,j} \qquad \text{for } c_{i,j} > 1 \,,$$

$$B_j = \sum_{i=1}^{I} m_i \cdot c_{i,j} \qquad \text{for } c_{i,j} = 1 \,,$$

$$\text{TOTAL}_{j_{(N)}} = \text{TOTAL}_{j_{(0)}} + \sum_{n=1}^{N} \left[\sum_{p=1}^{P} \Delta \text{MIN}_{p_{(n)}} \cdot b_{p,j} \right] .$$

The other unknowns (pH, pe, MIN, and ALK) are not adjusted until the mass balance criteria are satisfied within at least 20 percent.

The variables other than the activities of the master species of the elements are adjusted using a matrix technique. A modified Newton-Raphson method is used to linearize the set of nonlinear equations. The change in molality of each species relative to the changes in activities of the master species is given by taking the differential of the equations for the molality of species. If

$$m_i = \frac{K_i}{\gamma_i} \cdot \prod_{j=1}^{J} (a_j)^{c_{i,j}}$$

then the differential can be written:

$$\Delta m_i = \sum_{j=1}^{J} m_i \cdot c_{i,j} \cdot \frac{\Delta a_j}{a_j} \qquad \text{for each } i.$$

This formulation for the change in molalities of each aqueous species is linear in the quantities

$$\frac{\Delta a_j}{a_j} \,.$$

The differential of the electrical balance equation (equation 1 in the previous section) is:

$$\Delta\,\text{ELECT} = \sum_{i=1}^{I} z_i \cdot \Delta m_i \,.$$

At each iteration Δ ELECT must be the charge imbalance calulated from the distribution of species.

$$\Delta \mathrm{ELECT} = \sum_{i=1}^{I} z_i \cdot m_i \quad .$$

Taking the differential of the electron balance equation (equation 2) gives:

$$\Delta \mathrm{THOR} = - \sum_{p=1}^{P} u_p \cdot \Delta \mathrm{MIN}_p + \sum_{i=1}^{I} v_i \cdot \Delta m_i$$

where Δ THOR is the difference between the OPV state of the solution at a given iteration and the OPV state the solution should have at that iteration, V.

$$\Delta \mathrm{THOR} = V - \sum_{i=1}^{I} v_i \cdot m_i$$

and

$$V = \mathrm{OPV} + \sum_{n=1}^{N} \left[\sum_{p=1}^{P} u_p \cdot \Delta \mathrm{MIN}_{p_{(n)}} \right] \quad .$$

V is the OPV state of the initial solution plus the change resulting from the precipitation or addition of minerals.

The differential of a mass balance equation is:

$$\Delta \mathrm{TOT}_j = \sum_{i=1}^{I} c_{i,j} \cdot \Delta m_i - \sum_{p=1}^{P} b_{p,j} \cdot \Delta \mathrm{MIN}_p \quad .$$

At each iteration $\Delta \mathrm{TOT}_j$ is known to be:

$$\Delta \mathrm{TOT}_j = \mathrm{TOTAL}_{j_{(N)}} - \left[\sum_{i=1}^{I} c_{i,j} \cdot m_i \right]_{(N)} \quad ,$$

where,

$$\mathrm{TOTAL}_{j_{(N)}} = \mathrm{TOTAL}_{j_{(0)}} + \sum_{n=1}^{N} \left[\sum_{p=1}^{P} b_{p,j} \cdot \Delta \mathrm{MIN}_{p_{(n)}} \right] \quad .$$

That is, $\mathrm{TOTAL}_{j_{(N)}}$ is the initial total concentration of j plus any of the j^{th} element which has dissolved or precipitated in the previous iterations.

The mineral equilibrium equations are linearized by taking the total differential of the equation for the IAP of a mineral. That equation is:

$$\log \mathrm{IAP}_p = \sum_{j=1}^{J} b_{p,j} \cdot \log a_j$$

and the differential is:

$$\Delta \log \mathrm{IAP}_p = \sum_{j=1}^{J} b_{p,j} \cdot \frac{\Delta a_j}{a_j} .$$

Equilibrium imposes that

$$\Delta \log \mathrm{IAP}_p = \log K_p - \log \mathrm{IAP}_p = \log \frac{K_p}{\mathrm{IAP}_p} ,$$

therefore

$$\sum_{j=1}^{J} b_{p,j} \cdot \frac{\Delta a_j}{a_j} = \log \frac{K_p}{\mathrm{IAP}} \qquad \text{for each p.}$$

Now, because the Δm_i are linear with respect to $\frac{\Delta a_j}{a_j}$, all of the equations of differentials are linear in $\Delta \mathrm{MIN}_p$ and $\frac{\Delta a_j}{a_j}$. The coefficients for these variables are computed in the subroutine AQMOD. The system of equations is solved in SLNQ, and RESET computes new values for the major variables except for the activities of master species of the elements. For example,

$$a_{H^+_{(N+1)}} = a_{H^+_{(N)}} \cdot \left[1 + \frac{\Delta a_{H^+}}{a_{H^+_{(N)}}} \right]$$

and

$$MIN_{p_{(N+1)}} = MIN_{p_{(N)}} + \Delta MIN_{p_{(N+1)}} .$$

There are restrictions placed on the calculated deltas. The ΔMIN are reduced so that no negative total concentrations result. The pH and pe are not allowed to change more than 0.5 units. The total concentration of an element is not allowed to drop below 10^{-30} moles.

In some cases it is desirable to be able to adjust the initial solution to electrical neutrality at a constant pH. This can be achieved by setting IOPT(2) = 2. (See input section for details.) To solve this case, the program first solves the initial solution as if IOPT(2) = 0 (no adjustments for electrical balance) in order to determine the sign of the charge imbalance. Then, the electrical balance equation is used to calculate the activity of the properly charged species from NEUTRAL input which produces electrical neutrality. The mass balance equation for this species is not included in the set of equations which are solved. The total concentration for the NEUTRAL species used is determined by summing all the aqueous species for that element after electrical balance has been achieved.

When alkalinity is given instead of total carbon, the problem is again formulated slightly differently. In place of a mass balance on carbon there is an equation for alkalinity,

$$\sum_{i=1}^{I} A_i \cdot m_i = ALK,$$

where A_i is the number of equivalents contributed to the total alkalinity by a mole of the i^{th} aqueous species and ALK is the given total alkalinity. The values of A_i are by necessity an arbitrary approximation. To truly calculate the total carbon from alkalinity, the endpoint of the alkalinity titration must be known and all of the other analytical data must be perfect. Given imperfect analyses there is no way to distinguish the true alkalinity from the charge imbalance due to analytical error. In our data base (Attachment A) we have chosen pH 4.5 as our end point to agree with the USGS standard methods. We have arbitrarily included in the alkalinity only species with an H^+ dissociation reaction pK greater than 4.5. This is only an approximation since some species ($Al(OH)_3^o$, for example) would not be completely dissociated at pH 4.5 even though their entire molalities were considered as contributing to the alkalinity at the original solution pH. The program will accomodate different endpoints and different choices in alkalinity species via the input ALKSP (for each aqueous species) in the data base. This approach is satisfactory if the carbonate system dominates the measured titration alkalinity, but we emphasize that it is only a compromise for solutions in which the measured titration alkalinity contains significant contributions from species of iron, aluminum, or other elements.

One further caution concerning alkalinity should be noted. It is not possible to input the total alkalinity and then adjust the solution to electrical neutrality using pH. This is a theoretical impossibility, not a program limitation. Since alkalinity is in a sense a measure of negative charge, by fixing the alkalinity the total negative charge is fixed and, through the other analyses, the total positive charge is determined. If they are not equal adjusting the pH will not have any effect on the charge imbalance.

DESCRIPTION OF INPUT

PHREEQE is designed to perform a sequence of simulations in a single computer run. Each simulation consists of two separate problems:

1. Process an initial solution or solutions and

2. Model a reaction (starting from the initial solution(s)).

Many pathways for a simulation are accessable with a card input data deck; that is, no program modification should be necessary. Required input begins with a title card followed by an option card. Depending on the options selected, additional data are supplied using various "Keyword" data blocks. A data block consists of a Keyword card followed by appropriate data. The Keyword informs the program of the type and format of the data to follow. ELEMENTS and SPECIES, if they are used, should be the first two data blocks while the other keyword blocks may follow in any order. The keyword END denotes the end of the input data and is required once for each simulation. After the calculations for one simulation are completed, the program starts the data input process again, beginning with a new title and option card.

The general types of reactions that can be simulated are as follows:

1. Mixing of two solutions.

2. Titrating one solution with a second solution.

3. Adding or subtracting a net stoichiometric reaction (changing total concentrations of elements in proportion to a given stoichiometry).

4. Adding a net stoichiometric reaction until the phase boundary of a specified mineral is reached.

5. Equilibrating with mineral phases (mineral equilibrium can be specified with reaction types 1, 2, 3, 4, or 6 as well). Any condition which can be written in the form

$$\log (K_p) = \sum_i b_{p,i} \cdot \log (a_i),$$

where

a_i is activity of the i^{th} aqueous species,

$b_{p,i}$ is the stoichiometric coefficient of the

i^{th} aqueous species in the p^{th} phase, and

K_p is the equilibrium constant for the p^{th} phase,

is considered a mineral phase. This definition of mineral equilibrium includes the following:

a. Maintaining the aqueous phase in equilibrium with one or more minerals, such as calcite, $Fe(OH)_3$, or gypsum;

b. Equilibration of a mineral-water system with a gas (CO_2, CH_4, H_2S);

c. Apparent ion exchange in the sense that a ratio of two aqueous ion activities is kept constant.

Any combination of the above can be included in the MINERALS keyword input provided the Gibbs Phase Rule is not violated.

6. Changing temperature.

These six types of reaction (processes) may be used in various combinations. For example, one could add a net stoichiometric reaction to a starting solution while maintaining mineral equilibrium and increasing temperature.

In each type of reaction, an initial solution must be specified. There are three ways to provide a starting solution for a reaction. (1) The total concentrations of elements (and other necessary information such as pH, and temperature) may be input using the SOLUTION n keyword. n is either 1 or 2 and indicates the number of the array where the solution data will be stored. Any stoichiometric reaction or simple mineral equilibration is performed on solution number 1 alone. Solution number 2 is required only for mixing and titrating. (2) The second method of providing a starting solution for a reaction is to save the final solution from the reaction step of the previous simulation (provided more than one simulation is made in a run). IOPT(7) is used to specify the solution number into which the final solution will be saved. In the subsequent simulation no new solution should be read into that solution number. (3) Finally, if no reaction solution is saved and no new solutions are input, the solutions from the previous simulation remain in memory. Thus, a solution can be input once but can be used as the starting solution for several simulations.

One of the principle applications of PHREEQE is intended to be simulation of reactions based on observed water analyses, which will generally show an apparent electrical imbalance as a result of analytical errors. Because we use the electrical neutrality criterion in solving for pH, it is important to consider this apparent charge imbalance. Various options are available to achieve charge balance or to maintain a charge imbalance in the computations. Care should be taken in choosing the appropriate option and interpreting the results. Only perfect chemical analyses would produce electrical neutrality in an initial solution. Lacking these, the solution may be left electrically unbalanced by setting IOPT(2) = 0. When a reaction is modeled the final calculated solution will have the same electrical imbalance as the initial solution. If IOPT(2) = 1, the pH of the initial solution will be adjusted to produce electrical neutrality in that solution. It may be that the pH of the initial solution is well known and it is more reasonable to add relatively inert ions like K^+ or Cl^- to balance the solution electrically. In this case set IOPT(2) = 2, and use the keyword NEUTRAL and associated input to specify K and Cl. The amount of Cl or K added will be listed in the output. One final alternative is to attribute the charge error to the most suspect analysis, e.g. carbon or sodium, or to a constituent known to be present for which one has no analytical data. Again, set IOPT(2) = 2 and use the NEUTRAL input. Lack of charge balance is a meaningful clue to the errors in analyses and a large error probably makes a solution unsuitable for reaction simulation. By using the various options of the program, one can investigate the significance of analytical errors and their effects on reaction simulations. (Detailed test problems and examples for using PHREEQE are given in the section Test Problems.)

In the following description of the card input, the Fortran format for each card is given. Any Fortran manual will provide a complete explanation of the symbols used in format statements. Briefly, A indicates an alphanumeric character field, I an integer field, F floating point, E single precision exponential, D double precision exponential, and X indicates spaces. The first number following A, I, D, E, or F defines the length of the field, or the number of columns on the card reserved for the field. All integers must be right justified in their fields. All exponential fields, when including an exponent, must be right justified. For floating point and exponential fields, it is suggested that the decimal point always be included. A number preceding a letter is the repeat counter and indicates the number of times the field occurs consecutively on the card. Similarly a number directly preceding a parenthesis indicates the number of times the formats contained within the parentheses are repeated as a group. Any blanks in I, F, E, or D fields are considered to be zeros.

A. Title and option cards.

1. TITLE CARD TITLE
   FORMAT (20A4)
   Eighty characters of titles or comments.

2. OPTION CARD (IOPT(I), I = 1,9), NSTEPS, NCOMPS, V0
   FORMAT (9I1, 1X, 2I2, 6X, F10.5)

IOPT(1) = 0, No print of thermodynamic data or coefficients of aqueous species.

= 1, Print the aqueous model data (which are stored on disk) once during the entire computer run.

IOPT(2) = 0, Initial solutions are not to be charge balanced. Reaction solutions maintain the initial charge imbalance.

= 1, pH is adjusted in initial solution(s) to obtain charge balance.

= 2, The total concentration of one of the elements (except H or O) is adjusted to obtain electrical balance. NEUTRAL input is required.

IOPT(3) = 0, No reactions are modeled. Only the initial solutions are solved.

= 1, Solution 1 is *mixed* (a hypothetical constant volume process) with solution 2 in specified reaction steps. STEPS input and a value for NSTEPS are required. MINERALS input may be included.

= 2, Solution 1 is *titrated* with solution 2 in specified reaction steps. STEPS input, a value for NSTEPS, and a value for V0 are required. MINERALS input may be included.

= 3, A stoichiometric *reaction is added* in specified reaction steps. REACTION input, STEPS input, a value for NSTEPS, and a value for NCOMPS are required. MINERALS input may be included.

= 4, A net stoichiometric reaction is added in NSTEPS equal increments. REACTION input, STEPS input, a value for NSTEPS, and a value for NCOMPS are required. MINERALS input may be included. Only one value for the total reaction is read in STEPS.

= 5, Solution number 1 is equilibrated with mineral phases only. No other reaction is performed. MINERALS input is required.

= 6, A reaction is added to solution 1 until equilibrium is attained with the first phase in MINERALS input (equilibrium with other MINERALS phases is maintained throughout the reaction). REACTION input, a value for NCOMPS, and MINERALS input are required. No STEPS input is required. Note: there should be a common element in the reaction and the first phase in MINERALS input.

IOPT(4) = 0, The temperature of the reaction solution is (a) the same as the initial solution if adding a reaction, or (b) calculated linearly from the end members if mixing or titrating. No TEMP input required.

= 1, The temperature is constant during the reaction steps and differs from that of the initial solution(s). One value is read in the TEMP input.

= 2, The temperature is varied from T_o to T_f in NSTEPS equal increments during the reaction steps. A value for NSTEPS and two values of temperature, T_o and T_f, (in order) are required in the TEMP input, where T_o is the initial temperature and T_f is the final temperature.

= 3, The temperature of each reaction step is specified in TEMP input, in order. NSTEPS values are read.

IOPT(5) = 0, The pe from the initial solution is held constant during all the reaction steps for the simulation.

= 1, The pe of the reaction solution is determined by the reaction.

IOPT(6) = 0, Activity coefficients are calculated as follows:

- a. the WATEQ Debye-Hückel formula is used for all species with GFLAG = 1 (see SPECIES input below),
- b. the Davies formula is used for all species with no ion size parameter (DHA = 0, see SPECIES input),
- c. the extended Debye-Hückel formula is used for all species with an ion size parameter (DHA 0).

= 1, Activity coefficients are calculated as follows:

- a. the WATEQ Debye-Hückel formula is used for all species with GFLAG = 1.
- b. the Davies formula is used for all other species.

IOPT(7) = 0, Do not save the aqueous phase composition at the end of a reaction for additional simulations.

= 1, Save the final reaction solution in solution number 1.

= 2, Save the final reaction solution in solution number 2.

IOPT(8) = 0, The debugging print routine is not called.

= 1, A long printout is output at each iteration in each problem. This print is to be used only if there are convergence problems with the program. (See Subroutine PBUG.)

IOPT(9) = 0, No printout of each array to be solved.

= 1, A long printout occurs of the entire array to be solved at each iteration. This print is used only if there are convergence problems. (See Subroutine SLNQ.)

NSTEPS The number of reaction steps. A value is required if IOPT(3) = 1, 2, 3, or 4, or if IOPT(4) = 2 or 3. (Right justified.)

NCOMPS	The number of constituents in a net stoichiometric reaction. A constituent may be any element with an index number between 4 and 30 inclusive. No aqueous species with index numbers greater than 30 may be included as reaction constituents except H_2 and O_2. Any constituent with an index number greater than 30 is assumed to be either H_2 or O_2 and has the effect of raising or lowering the redox state of the solution depending on the assigned valence (THMEAN). A value for NCOMPS is required if IOPT(3) = 3, 4, or 6. (Right justified.)
VO	The initial volume of solution number 1 when modeling a titration. The unit of VO must be the same as that of XSTEP (see STEPS input below) if IOPT(3) = 2. Otherwise, VO is not required.

B. Keyword data blocks. Blocks are preceded by a keyword card. The keywords are numbered and underlined in the following text. Each keyword must begin in the first column of the card. The appropriate cards, which are lettered in the text, must follow in order directly after the keyword.

1. ELEMENTS FORMAT (A8)

This input defines the names and indices of all elements in the aqueous model data base. One card 1.a is read for each element. The index numbers of the elements do not need to be consecutive or sequential. This input block must be terminated with one blank card. Generally these data will be part of the aqueous model stored on disk and read by the program at the beginning of each run. Only changes to the data base need to be in the input card deck.

1.a. TNAME, NELT, TGFW
FORMAT (A8,2X,I2,3X,F10.0)

TNAME	Alphanumeric name of element.
NELT	Index number assigned to the element. Number must be between 4 and 30, inclusive. (Right justified.)

TGFW Gram formula weight of the species used to report the analytical data. If solution data is to include alkalinity, TGFW for the element carbon must be the equivalent weight of the reported alkalinity species. TGFW is not used if the concentrations are entered as molality (IUNITS = 0 in SOLUTION input card 3.b).

1.b. Blank card.

2. SPECIES FORMAT (A8)

This input defines the names, index numbers and composition of all aqueous species in the aqueous model data base. Cards 2.a, 2.b, 2.c, and 2.d are read for each species. The index numbers for the species do not need to be sequential or consecutive. This input block must be terminated with one blank card. To eliminate a species (already in the PHREEQE data array) from the aqueous model only card 2.a followed by a blank card 2.b must be entered. More species changes could then follow or a second blank card would terminate this input block. All species must have association reactions which contain only master species (species numbers less than or equal to 30; see discussion in section, Equilibrium Equations). Reactions containing non-master species must be converted to master species reactions and the appropriate association constants must be calculated before they can be entered into the program. These data are generally stored in the disk file which is read by the program at the beginning of each run and retained for the entire run. Only changes and additions would appear in the input card deck.

2.a. I
FORMAT (I3)

I The index number assigned to the aqueous species. Numbers 4 through 30 are reserved for master species. 250 is the maximum index number for an aqueous species. (Right justified.)

2.b. SNAME, NSP, KFLAG,GFLAG, ZSP, THSP, DHA, ADHSP(1), ADHSP(2), ALKSP
FORMAT (A8,2X,I3,2I1,6F10.3)

Three different formulations are available for the activity coefficient expression.

i) Extended Debye-Hückel,

$$\text{Log } \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B \overset{o}{a}_i \sqrt{I}}$$

ii) WATEQ Debye-Hückel

$$\text{Log } \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I$$

iii) Davies

$$\text{Log } \gamma_i = -A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right),$$

where A and B in all three equations are constants depending on the dielectric constant of the solvent and the temperature (Robinson and Stokes, 1970).

SNAME Alphanumeric species name.

NSP The total number of master species in the association reaction that forms this species; do not count the species itself unless the species is a master species. (Right justified.)

KFLAG = 0, The Van't Hoff expression is used to calculate temperature dependence of the association constant for this species.

= 1, An analytical expression is used to calculate temperature dependence of the association constant. Values for ASP are required on card 2.c.

GFLAG = 0, The extended Debye-Hückel or Davies expression (according to IOPT(6)) is used to calculate the activity coefficient for this species if DHA >0 (see below). If DHA = 0 and GFLAG = 0, the Davies equation is always used regardless of IOPT(6).

	= 1, The WATEQ Debye-Hückel expression is used to calculate the activity coefficient of this species regardless of the value of IOPT(6).
ZSP	The charge on this aqueous species.
THSP	The sum of the OPV's of the redox species in this species. (e.g. $FeSO_4^o$ has a THSP = 2 + 6 = 8.)
DHA	The extended Debye-Hückel a_i^o term. If this parameter is zero and GFLAG = 0 then the Davies equation is used to calculate the activity coefficient for this species.
ADHSP(1)	The a_i term for the WATEQ Debye-Hückel expression.
ADHSP(2)	The b_i term for the WATEQ Debye-Hückel expression.
ALKSP	The alkalinity assigned to this aqueous species. (See discussion in Numerical Methods section.)

2.c. LKTOSP,DHSP,(ASP(I),I = 1,5)
FORMAT (2F10.3,5E12.5)
Constants used to evaluate the association constant as a function of temperature. The analytical expression has the form:

$$\mathrm{Log}(K) = A_1 + A_2 T + A_3/T + A_4 \log T + A_5/T^2$$

where T is expressed in °K.

LKTOSP	Log_{10} of the mass action association constant at 25°C (used in Van't Hoff equation).
DHSP	Standard enthalpy of the association reaction at 25°C (ΔH_r^o, in kcal/mole); used in the Van't Hoff calculation of the temperature dependence of the association reaction. Required if KFLAG = 0. (A zero or blank will result in no temperature variation in the association constant.)
ASP(1)	Constant term in the analytical expression for the association constant, (A_1). The array ASP is used if KFLAG = 1.

ASP(2)	Coefficient of $T^{o}K$ in analytic expression, (A_2).
ASP(3)	Coefficient of 1/T in analytic expression, (A_3).
ASP(4)	Coefficient of log T in analytic expression, (A_4).
ASP(5)	Coefficient of $1/T^2$ in analytic expression, (A_5).

2.d. (LSP(I), CSP(I), I = 1, NSP)
FORMAT 6(I3,F7.3)
List of master species numbers and their coefficients in the mass action association reaction. NSP pairs of values, LSP and CSP, are read. One and only one of these cards is required for each species.

LSP(I)	Index number of master species. (Right justified.)
CSP(I)	Stoichiometric coefficient of master species in this aqueous species.

For example, using the data base in Attachment A for master species, the reactions below define variables as shown:

$$Ca^{2+} + H^{+} + CO_3^{2-} = CaHCO_3^{+} \quad \text{(species 77)}$$

NSP = 3
LSP(1) = 4, CSP(1) = 1.0; LSP(2) = 1, CSP(2) = 1.0;
LSP(3) = 15, CSP(3) = 1.0.

$$SO_4^{2-} + 8H^{+} + 8e^{-} = S^{2-} + 4H_2O \quad \text{(species 41)}$$

or,

$$SO_4^{2-} + 8H^{+} + 8e^{-} - 4H_2O = S^{2-}$$

NSP = 4
LSP(1) = 16, CSP(1) = 1.0; LSP(2) = 1, CSP(2) = 8.0;
LSP(3) = 2, CSP(3) = 8.0; LSP(4) = 3, CSP(4) = -4.0.

2.e. Blank card.

3. SOLUTION n — FORMAT (A8,1X,I1)
This input is used to define a starting solution. n can be either 1 or 2 and indicates the solution number of the data following. Cards 3.a and 3.b are required. Card 3.c is not included if NTOTS = 0. There must be as many card 3.c's as necessary to read NTOTS total concentrations.

3.a. HEAD
FORMAT (20A4)
Title or comments about the solution.

HEAD Alphanumeric heading.

3.b. NTOTS, IALK, IUNITS, PH, PE, TEMP, SDENS
FORMAT (I2,I3,I2,3X,4F10.3)

NTOTS The number of total concentrations to be read from card 3.c input. For example, if the starting solution is a $MgCl_2$ - $NaHCO_3$ solution, NTOTS = 4 (for Mg, Cl, Na, and C). (Right justified.)

IALK Flag which indicates whether total carbon or total alkalinity is to be input. (Right justified.)

= 0 indicates the total concentration of carbon (not alkalinity) is input in the units specified by IUNITS (see below).

= n $4 \leq n \leq 30$, where n is the index number for the element carbon, (in our data base n=15) indicates total alkalinity is being entered. If alkalinity is used ($n > 0$), then IOPT(2) can not be equal to 1. It is theoretically impossible to use pH to achieve electrical neutrality if the alkalinity is fixed. ELEMENTS input may be required. The units of alkalinity are specified by IUNITS (below) and if IUNITS > 0, the gram formula weight (GFW) of the element carbon is critically important. The GFW in the case of alkalinity must be the gram equivalent weight (grams/equivalent) of the chemical species in which the alkalinity is reported. The following is a list of species commonly used for reporting alkalinity and their corresponding equivalent weights:

$CaCO_3$	50.0446 g/eq
HCO_3^-	61.0171 g/eq
CO_3^{2-}	30.0046 g/eq.

(Note that: Alkalinity (mg HCO_3/l) =
Alkalinity (mg $CaCO_3$/l) x 1.21925)

	In our data base 44.010 is the GFW of carbon which is suitable for entering carbon as total CO_2. This GFW must be changed via ELEMENTS input if alkalinity is to be entered as mg/l or ppm (IUNITS = 2 or 3). If IUNITS = 0 alkalinity must be input as eq/kg H_2O and in this case the GFW need not be changed because no conversion of units is necessary. For a discussion of the contribution of the different aqueous species to the total alkalinity see the Numerical Methods section.
IUNITS	Flag describing units of input concentrations (right justified). The program makes all of its calculations in terms of molality and any other allowed concentration units (mmoles/l, mg/l, or ppm) must be converted to molality before the calculations may begin. To make the conversions it is necessary to know the gram formula weight (GFW), in g/mole, of the chemical formula in which elemental analyses are reported. The GFW is an input parameter under ELEMENTS input and must be in agreement with the analytical units for each solution data set. (If the units are molality, no conversion is necessary and the GFW's are not used.) Consider silicon as an example: Si is commonly reported as ppm of SiO_2 but may also be given as ppm H_4SiO_4. To convert ppm SiO_2 to moles Si/kg H_2O the GFW for silicon in the ELEMENTS data must be 60.0843. For ppm H_4SiO_4 the GFW must be 96.1147. If the units of the water analysis do not correspond to the GFW for any element, the GFW must be changed using ELEMENTS input or the data must be converted by hand before input into the program. Values of GFW used in the preliminary PHREEQE data base are given in Table 1. Note: All elements must have the same units. It is not possible to enter mg/l of one element and molality of another.

= 0 Concentration of elements entered as molality of each element, or for alkalinity, equivalents/kg H_2O.

= 1 Concentration of elements entered as mmoles/l of each element, or for alkalinity, meq/l.

= 2 Concentration of elements entered as mg/l of the species which has a gram formula weight given in ELEMENTS input. (ELEMENTS input may be required.) For alkalinity see discussion under IALK above.

= 3 Concentration of elements entered as ppm of the species which has a gram formula weight given in ELEMENTS input. (ELEMENTS input may be required.) For alkalinity see discussion under IALK above.

= 4 Concentration of elements entered as millimoles per kilogram of solution, or for alkalinity as milliequilivalents per kg solution.

PH	The pH of the solution (the approximate pH if IOPT(2) = 1). Required for all solutions.
PE	The pe of the solution. Required for all solutions.
TEMP	The temperature of the solution in °Celsius.
SDENS	The density of the solution. Required if concentrations are input as mmoles/l, mg/l, or ppm. If SDENS is omitted, 1.0 is assumed.

3.c. (LT(I), DTOT(I), I = 1, NTOTS)
FORMAT 5(I4,D11.3)
Total concentrations of elements. Five values of LT and DTOT are read on each card. The card may be repeated in order to enter all the elements desired. All data must appear consecutively in the fields, no blanks or zeros are allowed as values for LT. Omit this card if NTOTS is zero, the case of pure water.

LT	Index number of the element. (Right justified.)
DTOT	Total concentration of the element in molality, mmoles/l, mg/l, or ppm according to IUNITS.

4. MINERALS FORMAT (A8)

This input defines the phases which will be maintained at equilibrium with each of the reaction solutions. Cards 4.a and 4.b are required for each mineral. Card 4.c is optional for each mineral depending on the value of MFLAG. Unlike SPECIES, MINERALS may be defined in terms of any aqueous species, not just the master species. The input expression for the equilibrium constant must correspond with the input mass action coefficients. Mineral reactions are written as dissociation reactions. MINERALS input must be terminated with a blank card.

4.a. MNAME, NMINO, THMIN, LKTOM, DHMIN, MFLAG,SIMIN
FORMAT (A8,2X,I2,3X,3F10.2,5X,I1,9X,F10.3)
Constant parameters for this mineral.

MNAME Alphanumeric name of mineral.

NMINO Number of different species in the mineral dissociation reaction (including H^+, e^-, and H_2O). NMINO must be less than or equal to 10. (Right justified.)

THMIN The sum of the OPV's of the species in the mineral dissociation reaction.

For example,

$$FeS_2 = Fe^{2+} + 2S^{2-} - 2e^-$$

$$THMIN_{Pyrite} = 1(+2) + 2(-2) - 2(-1) = 0$$

$$Fe(OH)_3 = Fe^{3+} + 3OH^-$$

$$THMIN_{Fe(OH)_3} = 1(+3) + 3(0) = +3$$

$$CaCO_3 = Ca^{2+} + CO_3^{2-}$$

$$THMIN_{CaCO_3} = 1(0) + 1(+4) = +4$$

LKTOM Log of the equilibrium constant at 25°C for the reaction.

DHMIN ΔH_r^o (kcal/mole) for the Van't Hoff expression.

MFLAG = 0, The Van't Hoff expression is used to calculate the temperature dependence of the equilibrium constant.

= 1, The analytical expression is used to calculate the temperature dependence of the equilibrium constant. Card 4.c is required.

SIMIN Saturation index (log(Ion Activity Product/K_{sp})) desired in the final solution. SIMIN = 0.0 would produce equilibrium with the mineral while 1.0 would produce a solution 10 times supersaturated (SI = 1.0). This variable is useful in specifying the partial pressure of a gas. The Henry's law constant for the gas would be entered using the Van't Hoff constant (LKTOM) or analytical expression (AMIN) and the log of the partial pressure would be entered for for SIMIN.

4.b. (LMIN(I), CMIN(I), I=1, NMINO)
FORMAT 5(I4,F11.3)
List of species index numbers and stoichiometric coefficients in the dissociation reaction for this mineral. NMINO pairs of numbers, LMIN and CMIN, are read. The maximum value of NMINO is 10. If NMINO is greater than 5, a second card 4.b is required.

LMIN(I) Index number of species (not necessarily master species) in the dissociation reaction for this mineral. (Right justified.)

CMIN(I) Stoichiometric coefficient of species in dissociation reaction.

For example, using the data for aqueous species index numbers in Attachment A,

i. $CaCO_3 = Ca^{2+} + CO_3^{2-}$

NMINO = 2
LMIN(1) = 4, CMIN(1) = 1.0;
LMIN(2) = 15, CMIN(2) = 1.0.

ii. $FeS_2 + 2e^- = Fe^{2+} + 2S^{2-}$

or,

$FeS_2 = Fe^{2+} + 2S^{2-} - 2e^-$

NMINO = 3
LMIN(1) = 8, CMIN(1) = 1.0;
LMIN(2) = 41, CMIN(2) = 2.0;
LMIN(3) = 2, CMIN(3) = -2.0.

iii. $CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

NMINO = 3
LMIN(1) = 4, CMIN(1) = 1.0;
LMIN(2) = 16, CMIN(2) = 1.0;
LMIN(3) = 3, CMIN(3) = 2.0.

iv. $Ca^{2+} - Na^+$ ion exchange. (Assumes composition of exchanger does not change.)

$Na_2(ex) + Ca^{2+} = Ca(ex) + 2Na^+$

or

$Na_2(ex) - Ca(ex) = 2Na^+ - Ca^{2+}$

NMINO = 2
LMIN(1) = 6, CMIN(1) = 2.0;
LMIN(2) = 4, CMIN(2) = -1.0.

LKTOM = $\dfrac{a^2_{Na^+}}{a_{Ca^{2+}}}$ at exchange equilibrium.

v. Fix CO_2 partial pressure.

$CO_{2(gas)} + H_2O = H_2CO_{3(aq)}$

or

$CO_{2(gas)} = H_2CO_{3(aq)} - H_2O$

NMINO = 2
LMIN(1) = 35, CMIN(1) = 1.0;
LMIN(2) = 3, CMIN(2) = -1.0,
LKTOM = Henry's law constant for CO_2,
SIMIN = Log P_{CO_2} desired.

4.c. AMIN(I), I = 1,5
FORMAT (5E12.5)
Equilibrium constant expression of the form:

$$\text{Log}(K) = A_1 + A_2\,T + A_3/T + A_4 \log T + A_5/T^2,$$

for the mineral dissociation reaction where T is $^{\circ}$K. This card is used only if MFLAG = 1.

AMIN(1)	Constant coefficient of analytical expression, (A_1 above).
AMIN(2)	Coefficient of T$^{\circ}$K in analytical expression, (A_2).
AMIN(3)	Coefficient of 1/T in analytical expression, (A_3).
AMIN(4)	Coefficient of log T in analytical expression, (A_4).
AMIN(5)	Coefficient of $1/T^2$ in analytical expression, (A_5).

4.d. Blank card.

5. LOOK MIN FORMAT (A8)

The purpose of this input is simply to provide information on the saturation state of the aqueous phase with respect to desired minerals. The minerals in this block of input do not affect the calculations of the initial solution or any of the reaction solutions. This input is never mandatory. The Ion Activity Product (IAP) and saturation index (SI = log (IAP/K)) of each of these minerals is printed in the output following each solution description. Only the minerals which contain elements present in the solution are printed. The input following this card is identical to the input for MINERALS (see above). This input must be terminated with a blank card.

The list of "look minerals" is maintained for the duration of the run and any new "look mineral" is simply added to the list. If a "look mineral" is added that has the identical 8 letter name as another mineral in the list, the new mineral replaces the old mineral. The word DELETE as a mineral name will eliminate all of the minerals in the list and new minerals may be added. Only thirty nine "look minerals" are allowed. LOOK MIN input is generally placed in the disk file which is read at the beginning of each run. The input card deck need only contain additions and changes to that permanent list.

6. TEMP

FORMAT (A8)
This input varies the temperature during the reaction steps. It is required input if IOPT(4) is greater than 0. Only one card 6.a is necessary unless IOPT(4) = 3. In that case as many cards as necessary to input NSTEPS values are required.

6.a. XTEMP
FORMAT (8F10.1)

XTEMP Temperature in degrees Celsius.
If IOPT(4) = 1, one value of XTEMP is coded.
If IOPT(4) = 2, two values of XTEMP are coded, T_o and T_f (in order).
If IOPT(4) = 3, NSTEPS values of XTEMP are coded (no blank fields permitted).

7. STEPS

FORMAT (A8)
This input defines the steps of the reaction process. The input has a different meaning depending on the value of IOPT(3) (option card).

IOPT(3) = 1, XSTEP is the fraction of solution 1 to be mixed with solution 2. NSTEPS values are read.

IOPT(3) = 2, XSTEP is the volume of solution 2 to be titrated into solution 1. XSTEP must have the same units as V0 (option card). NSTEPS values are read.

IOPT(3) = 3, XSTEP is the moles of reaction to be added to solution 1. NSTEP values are read.

IOPT(3) = 4, Only one value of XSTEP is read. XSTEP is the total number of moles of reaction to be added in NSTEPS steps. NSTEPS reaction solutions will be calculated. The Ith solution will have I·XSTEP/NSTEPS moles of reaction added to solution 1.

7.a. XSTEP
FORMAT (8F10.3)

XSTEP	Reaction increments as defined above.

8. REACTION FORMAT (A8)

This input describes the stoichiometry and valence of the elements to be added as a reaction. STEPS input (see above) defines the total number of moles of this reaction to be added. The REACTION process changes the total aqueous concentration of an element by the stoichiometric coefficient (CREAC) times the total moles of reaction (XSTEP). (However, the final total concentration in the reaction solution may also be altered by mass transfer to achieve equilibrium with minerals specified in MINERALS input.) It is necessary to consider the charge balance of the reaction which is added. A charge imbalance by an input error or by intent is equivalent to adding acid or base. If the reaction is a simulation from a known solution to another known solution it is possible to add an inert electrical charge equal to the difference in the charge imbalance between the two solutions. Set LREAC(I) = 0, CREAC(I) = Δ charge imbalance (equivalents/kgH_2O) and THMEAN(I)=0.0. This will eliminate implicit addition of acid or base. Card 8.a is repeated as often as necessary to read NCOMPS (option card) reaction constituents.

8.a. (LREAC(I), CREAC(I), THMEAN(I), I = 1,NCOMPS)
FORMAT 4(I4,2F8.3)

This input defines a net stoichiometric reaction. Four triples of numbers are read on each card. Enough cards must be included to read NCOMPS triples of numbers.

LREAC(I)	Index number of element for the reaction. LREAC must be between 4 and 30 inclusive. If LREAC is greater than 30 the program considers this constituent to be H_2 or O_2 and only uses CREAC and THMEAN (below) to change the oxidation state of the reaction solution. (Right justified.)

CREAC(I)	Stoichiometric coefficient of the element in the reaction.
THMEAN(I)	The OPV of the element in the reaction (e.g. carbon as carbonate: THMEAN = +4; carbon as methane: THMEAN = -4; ferrous iron: +2; and ferric iron: +3). An element may be included more than once in a reaction to accomodate different valence states of the element.

The variables which affect a reaction simulation are IOPT(3), NSTEPS, and NCOMPS from the option card, REACTION input and STEPS input. The following examples use the species index numbers from Attachment A.

i. Gypsum is added to the initial solution in 5 equal increments of 0.005 moles, to a total of .025 moles. Calcite equilibrium is maintained in each of the five steps.

IOPT(3) = 4 (net reaction added linearly).
NSTEPS = 5 (5 reaction steps).
NCOMPS = 2 (2 constituents, Ca and S).
LREAC(1) = 4, CREAC(1) = 1.0, THMEAN(1) = 0.0 (Ca),
LREAC(2) = 16, CREAC(2) = 1.0, THMEAN(2) = 6.0 (S).
MINERALS input, calcite.
XSTEP(1) = .025 (total moles of reaction to be added).

The total calcium at the completion of the first reaction step is given by:

$$Ca_{tot} = Ca_{tot(initial)} + .005 + MIN_{calcite} .$$

ii. Suppose mass balance between two solutions shows calcite, gypsum, and dolomite dissolving (+) and precipitating (-) in proportions of -1:1.5:1. The net reaction is written:

- 1 Ca			- 1 C		Calcite
+ 1.5 Ca				+ 1.5 S	Gypsum
+ 1 Ca	+	1 Mg	+ 2 C		Dolomite
1.5 Ca	+	1 Mg	+ 1 C	+ 1.5 S	NET

Three points along this possible path are modeled by (arbitrarily) adding 10^{-4}, 10^{-3}, and 10^{-2} moles of the net reaction.

IOPT(3) = 3 (add net reaction in specified steps).
NSTEPS = 3 (number of steps).
NCOMPS = 4 (number of constituents in the reaction).
LREAC(1) = 4, CREAC(1) = 1.5, THMEAN(1) = 0.0 (Ca);
LREAC(2) = 5, CREAC(2) = 1.0, THMEAN(2) = 0.0 (Mg);
LREAC(3) = 15, CREAC(3) = 1.0, THMEAN(3) = 4.0 (C);
LREAC(4) = 16, CREAC(4) = 1.5, THMEAN(4) = 6.0 (S).
XSTEP(1) = 10^{-4}, XSTEP(2) = 10^{-3}, XSTEP(3) = 10^{-2}.
(Reaction increments in moles, reaction is not cumulative.)

9. <u>NEUTRAL</u> FORMAT (A8)

This input defines the elements to be used to adjust the initial solution(s) to electrical neutrality. One element with a master species cation and one element with a master species anion are input. H^+ and e^- are not valid entries. A master cation and anion are required in order to <u>add</u> one or the other element according to the charge imbalance. Species are not <u>subtracted</u>, eliminating the possibility of negative total concentrations. This input is required only if IOPT(2) = 2. (Note that this is <u>not</u> equivalent to adding or subtracting charge as discussed in REACTION; remember that IOPT(2) = 0 will maintain an original charge imbalance during a simulation.)

9.a. LPOS, LNEG
FORMAT (2I5)

LPOS	Index number of an element with a cation master species. (Right justified.)
LNEG	Index number of an element with a anion master species. (Right justified.)

10. <u>SUMS</u> FORMAT (A8)

This input sums molalities of aqueous species which are then printed in the output of the run. These sums do not affect the calculations in any way and are never mandatory. These sums could, for example, be used to define an alternate sum of species for the alkalinity. The "sums" are defined by lists of species numbers, so that each time a sequence number for a species is listed, the sum is incremented by the molality of that species. If the species has, for example, two carbonate ions and the total carbonate is the sum which is desired then the species should be listed twice in that sum. Up to 10 different sums may be defined. Each sum may have up to 50 species. Cards 10.a and 10.b are required for each sum. This input, after all sums have been defined, must be terminated with one blank card.

As in LOOK MIN input the sums are kept for the duration of the run but it is possible to add or replace sums or delete the entire set in any single simulation. Any sum input in this data block will be added to the list of sums if the name (SUNAME) is different from all other sum names. A sum with the identical name will replace the sum already in the list. The word DELETE as a sum name will eliminate all the sums known to the computer.

10.a. SUNAME, NSUM
FORMAT (A8,2X,I2)

SUNAME	Alphanumeric name to be printed to identify the sum.
NSUM	The number of index numbers to be read on card(s) 10.b; NSUM 50. (Right justified.)

10.b. (LSUM(I,J), J = 1, NSUM)
FORMAT (20I4)
List of species numbers to define the sum. Twenty index numbers are read on this card. The card may be repeated as many times as necessary to input NSUM index numbers.

LSUM	Index numbers of species in sum. (Right justified.)

Note: repeat cards 10.a and 10.b for each sum.

10.c. Blank card. One blank card at the end of all sums is required to terminate this input.

11. KNOBS FORMAT(A8)

This input allows modification of some of the convergence criteria of the program. In particular, DMAX, DMIN, RMAX, and RMIN allow setting the maximum steps taken at each iteration for changes in pH and pe and for changes in the activities of the master species. CNVRG1, CNVRG2, and CHKMU modify the interaction of the two numerical methods, the Newton-Raphson and the continuation method. The maximum number of iterations allowed for a single simulation is controlled by ITMAX. KNOBS input is optional and is intended to be used only if

there are convergence problems. In general, smaller step sizes adjusted by DMAX, DMIN, RMAX, and RMIN will be more reliable at the expense of program speed. Adjustments to these variables and to ITMAX should be made first. Adjustments to the other variables is probably only necessary at very high ionic strengths where the theoretical basis for the ion association model is dubious. The default values used by the program are listed below.

11.a. DMAX, DMIN, FUDGE, RMAX, RMIN, CNVRG1, CNVRG2, ITMAX, CHKMU
FORMAT (*) free format.

DMAX This parameter is numerically related to the largest allowable decrease in pH and pe in one iteration. The formula for obtaining the maximum decrease is -log10(1+DMAX). The default value for DMAX is 10.0. The suggested range for this variable is 0.4 to 20.0. Smaller values will cause the program to converge more slowly. The corresponding maximum pH decreases for several values of DMAX are listed here.

DMAX	maximum allowed decrease in pH and pe
20.0	-1.32
10.0	-1.04
5.0	-0.78
1.0	-0.30
0.4	-0.15

DMIN This parameter is numerically related to the largest allowable increase in pH and pe in one iteration. The formula for obtaining the maximum increase is -log10(1-DMIN). The default value for DMIN is 0.7. DMIN must be between 0.0 and 1.0, exclusive of the extremes. Small values will cause the program to converge more slowly. The corresponding maximum pH increases for several values of DMIN are listed here.

DMIN	maximum allowed increase in pH and pe
0.1	0.05
0.3	0.15
0.5	0.30
0.7	0.52
0.9	1.00

FUDGE is not used in this version of PHREEQE. It is set internally by the program.

RMAX is related to the maximum increase in the log of the activities of master species other than pH and pe. The quantity log10(RMAX+1) is the maximum log increase in the activities of master species allowed per iteration. The default value of RMAX is 20, corresponding to a maximum increase of 1.32 log units in the activity of master species in one iteration. The correspondence between values of RMAX and maximum log increases in activity is the same as given above for DMAX except that the sign is positive. (If DMAX is interpreted in terms of log10(aH+), the parallel is exact.) The suggested range of RMAX is between 0.5 and 20.0. Small values will cause the program to convergence more slowly.

RMIN is related to the maximum decrease in the log of the activities of master species other than pH and pe. The quantity log10(1-RMIN) is the maximum log decrease allowed in the activities of the master species per iteration. RMIN must be between 0.0 and 1.0, exclusive of the extremes. The default value of RMIN is 0.9 corresponding to a maximim decrease in the log of the activities of the master species of -1.0. The correspondence between RMIN and the maximum log decrease is the same as that given for DMIN above, except the sign is positive.

CNVG1 This parameter applies to the Newton-Raphson technique. PHREEQE requires the mass balance equations to be solved within a given criterion before the electrical balance, electron balance, and mineral equilibria equations are included. CNVG1 is the fractional error in mass balance allowed when including the other equations. The default value of CNVG1 is 0.1, implying that if more than a 10 percent error is detected in any of the mass balance equations, the additional equations are not included in that iteration.

CNVG2 This parameter applies to the continuation numerical method. PHREEQE requires the mass balance equations to be solved within a given criterion before the Newton-Raphson technique is used. CNVG2 is the fractional error in mass balance allowed when invoking the Newton-Raphson method. The default value is 10000.0, implying that the Newton-Raphson method is used almost exclusively. In some problems, the Newton-Raphson method does not converge because the initial estimates of the activities of the master variables are not close enough to the true activities. Setting CNVG2 to a number between 0.001 and 1.0 may help. This would cause the program to use the continuation method to find a solution to the mass balance equations (within the limit set by CNVG2) before the Newton-Raphson method is used.

ITMAX This variable sets the maximum number of iterations allowed on any simulation before the program stops. The default value is 200 iterations.

CHKMU This variable is compared to the change in ionic strength between iterations. If the ionic strength is changing by more than the fractional value of CHKMU, then no method is used and the same values of the master variables are used in the next iteration. The default value of 0.1 implies that until the ionic strength is constant within 10 percent, no changes will be made in the master variables. Sometimes it helps to have the ionic strength stabilized like this and sometimes it leads to oscillations where the change in activity coefficients is large enough to change the ionic strength by a considerable amount. These problems generally occur at high ionic strengths where the reliability of the program is questionable under any circumstances.

12. <u>END</u> FORMAT (A8)

This card terminates input operations for a single simulation. Initial solution(s) and reaction solution(s) are computed as directed by the preceeding input. Any computer run has at least one END card.

THERMODYNAMIC DATA BASE

Modeled results from PHREEQE are no better than the thermodynamic data on which they are based. A preliminary thermodynamic data base is given in Attachment A and includes 120 aqueous species (SPECIES input) of 19 elements (ELEMENTS input). A preliminary LOOK MIN data base for 24 minerals (including P_{CO_2}) is also given. The thermodynamic data base has been adopted from various sources, but largely from the recent compilation of Ball and others (1979) and Ball and others (1980) in the equilibrium model WATEQ2. In the preliminary data base the Debye-Hückel ion size parameters (variable DHA) are taken from Kielland (1937) when available. All other ion size parameters are zero. (See IOPT(6) on input card A.2.) A comparison of the aqueous model of WATEQ2 with other models in current use is given by Nordstrom and others (1979).

Although the PHREEQE data base given in Attachment A has been extensively tested against results from WATEQ2 and WATEQF (Plummer and others, 1976), it 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.

Organization Rules

Because the thermodynamic data base is defined separately from the PHREEQE source code, the data base can be extensively altered provided a few basic rules of its organization are followed. (1) The data base for the aqueous phase is formulated in terms of an ion-pairing model. (2) The appropriate data must be represented according to the formats described earlier under ELEMENTS, SPECIES, and LOOK MIN (see MINERALS) input. (3) The maximum number of elements that may be included in a data base is 27. Index numbers for the elements must be greater than or equal to 4 but less than or equal to 30. The index numbers for the elements do not need to be consecutive or sequential. (4) The maximum index number of a species is 250. SPECIES numbers 1, 2, and 3 are required to be H^+, e^-, and H_2O. There are no element numbers corresponding to species 1, 2, and 3. SPECIES 4-30 are designated master species. There is one master species for each element and the index number of a master species is that of the corresponding element. SPECIES 31-250 represent other ions, complexes, or ion pairs which are defined by ion association reactions involving species 1-30. (See description of SPECIES input.) (5) LOOK MIN cards are optional, but if included are limited to a maximum of 39 minerals.

Changing the Data Base

Changes to the preliminary data base (Attachment A) can be made with the input cards through use of ELEMENTS, SPECIES, and LOOK MIN input. The more common types of changes to the preliminary data are as follows:

1. Changing the value of the gram formula weight (GFW) of an analyzed (input) constituent in solution.

Table 1 lists the elements, gram formula weights, and OPV used in the preliminary data base (Attachment A). Because conversion of the analytical units of a water composition in ppm or mg/l to the unit of molality (used internally by PHREEQE) depends on the gram formula weight of the analyzed constituent, it is necessary to have each element consistent with the stoichiometric formula for which it is reported in the analysis. For example, silicon (element number 13, Table 1) is sometimes reported as Si (GFW = 28.0855) rather than SiO_2 (GFW = 60.0848 in preliminary data base for PHREEQE). In order to use the reported analysis as Si, one could use ELEMENTS input to redefine the gram formula weight as 28.0855, rather than 60.0848 (SiO_2).

Using the data base in Attachment A, dissolved inorganic carbon in the starting solution must be entered as total CO_2 (GFW = 44.0098). If total titration alkalinity is entered (see IALK input under keyword SOLUTION), it is necesary to use ELEMENTS input to change the pre-set gram formula weight of CO_2 to the appropriate value of the equivalent weight in which the alkalinity is given. For example, if total titration alkalinity is given as mg/l $CaCO_3$, the following input is required: (1) ELEMENTS input to change the GFW of carbon (species number 15 in the preliminary data set) to 50.0446 (equivalent weight of $CaCO_3$), (2) SOLUTION n input must show IUNITS = 2 (mg/l), and IALK = 15. (See Description of Input section, keyword SOLUTION n, for an explanation of IALK and IUNITS. See the Numerical Methods section for a discussion of our definition of total alkalinity.)

2. Adding a new element to the data set.

In order to make PHREEQE calculations with a new element not already present in the PHREEQE data set (Attachment A), ELEMENTS input is required to a) define the name of the element, b) the element number, and c) the gram formula weight in which the analytical data for the element are reported. In addition, for each new element appropriate SPECIES cards are required to define the ion-association model for that new element.

Table 1. - Elements data

Element	Number	Gram formula weight	Input formula corresponding to gram formula weight	Master species	Operational valence
Ca	4	40.08	Ca^{2+}	Ca^{2+}	0
Mg	5	24.305	Mg^{2+}	Mg^{2+}	0
Na	6	22.9898	Na^{+}	Na^{+}	0
K	7	39.0983	K^{+}	K^{+}	0
Fe	8	55.847	Fe^{2+}	Fe^{+2}	+2
Mn	9	54.9380	Mn^{2+}	Mn^{2+}	+2
Al	10	26.9815	Al^{3+}	Al^{3+}	0
Ba	11	137.33	Ba^{2+}	Ba^{2+}	0
Sr	12	87.62	Sr^{2+}	Sr^{2+}	0
Si	13	60.0843	SiO_2	H_4SiO_4	0
Cl	14	35.453	Cl^{-}	Cl^{-}	0
C	15	44.0098	CO_2	CO_3^{2-}	+4
S	16	96.06	SO_4^{2-}	SO_4^{2-}	+6
N	17	62.0049	NO_3^{-}	NO_3^{-}	+5
B	18	10.81	B	H_3BO_3	0
P	19	94.9714	PO_4^{3-}	PO_4^{3-}	0
F	20	18.9984	F^{-}	F^{-}	0
Li	21	6.941	Li^{+}	Li^{+}	0
Br	22	79.904	Br^{-}	Br^{-}	0

The required SPECIES input for a new element is identification of a master species (numbers 4-30) with number corresponding to the element number. (See SPECIES input.)

3. Adding a new species

Once an element (ELEMENTS, numbers 4-30) and its master species (SPECIES, numbers 4-30) are defined, new species involving that element may be added to the data set when written as ion association reactions involving species 1-30. The number assigned to a species (31-250) must be unique, but the order in which species are numbered need not be consecutive. The numbering assigned to the species is used in the sequence of printing the distribution of species.

4. Deleting a species from the data base.

For each species deleted from the data base, one card of type 2.a (identifying the species number) followed by 1 blank card is required under SPECIES input. The last card of SPECIES input is, as always, a blank card (in addition to that for species deletion).

5. Changing SPECIES data.

The thermodynamic data base will always be in a state of revision. The data for each species include information for calculating the individual ion activity coefficient, log K, and standard enthalpy of reaction for the formation of the species from the master species (species numbers 1-30). To change any part of the data base for a particular species requires reading the complete set of SPECIES input cards for that species (cards 2.a, 2.b, 2.c, and 2.d if KFLAG is 1; see description of SPECIES input). Note that if the master species for a particular element (species 4-30) is ever changed to another species of the same element, all SPECIES data defining other complexes or ion pairs for that particular element will have to be revised to reflect the new association reactions from a new master species. Master species 1-3 (H^+, e^-, H_2O) may not be changed.

6. Optional data in data base.

LOOK MIN and SUMS data may be included in the data base but are not required. The preliminary data base includes LOOK MIN cards for 24 minerals. This complete LOOK MIN data set can be deleted by reading under LOOK MIN input the word DELETE in columns 1-6 of card 4.a followed by a blank card.

To replace the preliminary LOOK MIN data set with a new one, again read DELETE followed by the new LOOK MIN data set which may contain up to 39 minerals. As many as 15 new minerals may be added to the existing LOOK MIN data base by simply including the new mineral cards (types 4.a and 4.b) under the LOOK MIN keyword. The last card under LOOK MIN input is always blank. Although no SUMS cards are included in the preliminary data base, SUMS cards may be included and updated in a manner identical to LOOK MIN cards.

PROGRAM LIMITATIONS

PHREEQE is an extremely general geochemical model and is applicable to most hydrochemical environments. There are, however, several conceptual and numerical limitations which must be considered.

Water (Masses of H and O)

Perhaps the single most important set of limitations on the calculations presented in this manual results from the fact that PHREEQE deals with masses of elements in terms of their concentrations in the aqueous phase and uses electrical neutrality and electron balance relations to complete the set of equations needed to solve a given problem. A consequence of this is that the masses of H and O are not considered in the numerical solution to our set of simultaneous equations. Although this does not pose a significant problem in the vast majority of systems to which PHREEQE will be applied, there are certain artifacts of the computations that can, under certain circumstances, be misleading. These are discussed below.

The basis for the mathematical treatment used here lies in the historical development of PHREEQE, namely its derivation from WATEQ and MIX2. For other computational approaches that include mass balance on O and H see Helgeson, and others (1970), or Wolery (1979).

1. Formation of O_2 and/or H_2

An obvious potential problem stemming from the lack of mass balance on O and H lies in working with redox systems involving chemical reactions that produce or consume H_2 or O_2. Because the only constraints on H_2 and O_2 in the calculations are equilibrium and electron balance constraints, there are no numerical limits on the amounts of H_2 or O_2 that can be made or destroyed (mathematically) to satisfy the constraint in a given simulation. If the masses of H_2 and O_2 involved in chemical reactions become significant relative to 1 kg of water, then the simulations may begin to deviate significantly from reality.

In dealing with natural geochemical environments we are generally limited by nature to environments that fall within the electrochemical stability field of water. At one atmosphere partial pressure of H_2 the solubility of the gas is on the order of 1 mmole/l, similarly the solubility of O_2 is also about 1 mmole/l. Thus, in simulation of closed-system reactions, the numerical errors involved in neglecting the formation of H_2 or O_2 from water are negligible - considerably less than 0.01 percent of the water present in the system. Errors involved in simulation of open-system processes must be evaluated on an individual basis; however, our feeling is that O_2/H_2 errors involved in modeling natural systems will in general be small. If, on the other hand, PHREEQE were to be applied to problems in corrosion chemistry or electrochemistry that involve significant dissociation of water, significant differences between computer simulations and real systems may arise.

2. Hydrated minerals

A second, and generally more significant, problem occurs if PHREEQE is used to model systems in which large amounts of water are involved in mineral precipitation or dissolution. The most obvious examples are reactions occurring in brines; for example, equilibrium phase-boundary precipitation of 1 mole of natron ($Na_2CO_3 \cdot 10H_2O$) from 1 liter of solution would remove 10 moles of H_2O from the aqueous phase with a resulting increase in concentration of constituents other than Na and C of about 20 percent (independent of other reactions). This increase in concentration would not be taken into account in PHREEQE's present computation system.

The "concentration error" will be on the order of 20 percent, the actual errors introduced into the simulation may be greater, and will be more difficult to evaluate. These errors will result from the effect (unaccounted for by PHREEQE) of the loss of 10 moles of H_2O on both the activity of water and the activity coefficients of the various aqueous species. It is possible that these errors may cancel; on the other hand they may reinforce each other. In the latter case, the errors may become very significant. Thus, while PHREEQE is perfectly capable of making brine-type calculations, extrapolation of these calculations to the real world should be done on an individual basis, and with extreme caution.

3. Evaporation

A few specific comments on techniques of evaporation simulation runs, in addition to the above precautions, can be made at this time. There are basically two ways to approach the problem of evaporation from the point of view of computer coding, the choice depends entirely on operator convenience:

a. The dissolved salts can be added as reactions in the appropriate proportions, via REACTION. For example a solution containing

1 mmole each of Na^+, K^+, Cl^-, and NO_3^- could be "evaporated"

simply by adding Na^+, K^+, Cl^-, and NO_3^- in equimolar amounts to the desired concentration.

b. Evaporation can also be simulated by using the titration option (IOPT(3) = 2) and titrating the system with minus H_2O ($-H_2O$).

Convergence Problems

Due to the non-linear nature of the equations involved, on some problems the program may not converge. This is much more likely to occur in problems involving redox because of the fact that equilibrium concentrations of some species can vary by more than 100 orders of magnitude from a fully oxidizing to a fully reducing environment. In general the less the redox potential of the solution has to change during a simulation the better the convergence possibilities. If problems arise, alternative paths to the same final solution should be tried if possible. If some idea of the final solution characteristics is available, simply start the calculations with the same concentrations but at a pH and pe close to the final anticipated composition. Also make sure that the problem is truly a redox problem. If one is modeling an NH_4^+ solution and there is no need to consider NO_3^- or other valences of nitrogen, then the data base can be rewritten with NH_4^+ as the master species, eliminating all other valences of N, and the problem is considerably simpler for the program to solve. (See ELEMENTS and SPECIES input, and test problem number 1.)

The program has solved virtually all of the problems we have tried to date. However, there is no numerical method which guarantees convergence to a solution of these non-linear equations. (See description of KNOBS input.)

Ion Exchange

There are two limitations in the way PHREEQE deals with ion exchange - one primarily conceptual, the other numerical.

PHREEQE deals with ion exchange simply by fixing the activity ratio of the exchangeable species:

$$A_{(aq)} + B_{ex} \rightleftharpoons A_{ex} + B_{(aq)}$$

$$K'_{ex} = a_{B_{(aq)}} / a_{A_{(aq)}} = K_{ex} \frac{a_{B_{ex}}}{a_{A_{ex}}}$$

The use of K'_{ex} for a given exchange reaction is generally a necessity because of the lack of thermodynamic data to define $a_{B_{ex}}$ and $a_{A_{ex}}$ in the solid phase. The use of K'_{ex}, and thus a fixed ratio of $a_{B_{ex}} / a_{A_{ex}}$, is equivalent to assuming an infinite reservoir of exchanger with constant solid phase composition. This assumption is not as extreme as it first seems, because there are few natural environments for which sufficient laboratory and field data are available to define in detail exchange characteristics as a function of time and/or position.

A more important limitation in the use of K'_{ex} to describe exchange processes arises if it is desired to work with exchange reactions that involve two or more ions exchanging with the same third ion in solution. For example, consider the possibility of exchange of both Ca^{2+} and Mg^{2+} for Na^+ on an exchanger. The ratios $a^2_{Na^+(aq)} / a_{Ca^{2+}(aq)}$ and $a^2_{Na^+(aq)} / a_{Mg^{2+}(aq)}$ for a given $a_{Na^+(aq)}$ specify the $a_{Ca^{2+}(aq)} / a_{Mg^{2+}(aq)}$ ratio. However, difficulties can arise depending on which phase boundaries are specified in a particular problem. For example, in the above example, it would not be unreasonable to try to model the Ca, Mg - Na exchange reactions at equilibrium with calcite and dolomite. Numerically, this problem cannot be solved for the following reason. The exchange reactions, for a given $a_{Na^+(aq)}$, specify the $a_{Ca^{2+}(aq)} / a_{Mg^{2+}(aq)}$ ratio. Similarly, equilibrium with calcite and dolomite also specifies $a_{Ca^{2+}(aq)} / a_{Mg^{2+}(aq)}$. If the two ratios are not numerically equal, the system is not at equilibrium, and PHREEQE cannot solve the equations. On the other hand, if the two ratios are numerically equal, equilibrium obtains; however, in this case, the number of equations exceeds the number of unknowns and again PHREEQE cannot solve the equations (in this case the error message THE GIBBS PHASE RULE HAS BEEN VIOLATED will appear). In real-world systems the phase rule is not in fact violated; the necessary variability is provided by the fact that $a_{A_{ex}}$ and $a_{B_{ex}}$ can change because there is no physical constraint requiring constant exchanger composition.

Ways of circumventing this problem must be chosen by the operator to fit individual situations. For example, in the above case the problem might be dealt with by specifying equilibrium with Ca-Na exchange, Mg-Na exchange, and calcite, then adding dolomite as a reactant until the desired solution composition is reached.

Water Stability Limits

Although in principle PHREEQE's calculations are not limited to the water stability field, it should be pointed out that because O_2, H_2, and H_2O are coupled via mass-action equations, the only way the program can deal with solutions outside of the normal thermodynamic stability limits of water (1 atmosphere total pressure) is to invoke partial pressures of O_2 and H_2 greater than 1 atm. As these partial pressures vary exponentially with the departure of pe from the water stability boundary, calculated solution properties rapidly become physically meaningless for comparison with natural environments.

This also brings up another caution for the PHREEQE user - posing insoluble problems. Here we are referring not to mathematically insoluble problems, as in the ion-exchange section above, but to problems that approach physicochemical absurdity. For example, one might attempt to calculate the solubility of Fe (metal) at a pe of +10. PHREEQE would in all probability be unable to solve this problem because of the enormously high activity of $Fe^{3+}_{(aq)}$ required for equilibrium.

Thus, although no fundamental rules (such as the phase rule) are violated, the problem, as posed, violates physical, if not mathematical, reality and will almost certainly cause the program to fail to converge.

Titration and Mixing

In performing titration calculations, PHREEQE uses the relations

$$V_T = V_1 + V_2 ,$$

and

$$V_T m_i = V_1 m_i + V_2 m_i ,$$

where,

V = volume of solution,
m_i = total molality of element i in solution 1 or solution 2, and
T = total.

The problem here lies in the fact that the above equations are valid for volume and molarity or normality, but not for volume and molality. The errors introduced in these calculations will be proportional to to $\rho -1$, where ρ is the density of the solutions involved in the titration.

In general, the error involved here is negligible; however, again caution must be exercised in attempting to simulate processes that occur in brines.

Mixing problems are treated by PHREEQE in a physically hypothetical manner; the volume of solution is assumed constant, and the total molality of an element in the final solution is simply given by

$$m_{i_f} = x_1 m_{i_1} + x_2 m_{i_2}$$

where

m_{i_j} = molality of i in solution, j = 1 or 2

x_j = fraction of solution 1 and 2 mixed; $x_1 + x_2 = 1$

f = final.

Activity of Water

The activity of water function used by PHREEQE is the same as that used in WATEQ (Truesdell and Jones, 1974), taken originally from Garrels and Christ (1965). The empirical equation is

$$a_{H_2O} = 1 - 0.017 \sum_{i=1}^{I} m_i$$

where $\sum_{i=1}^{I} m_i$ is the sum of the molalities of dissolved anions, cations, and neutral species. For numerical purposes, PHREEQE has a lower numerical limit of 0.3 imposed, to prevent a_{H_2O} from approaching zero or going negative during intermediate iteration steps in which guesses on $\sum_{i=1}^{I} m_i$ might be very high.

Uniqueness of Solutions

A final precaution should be discussed at this point. This is really a general commentary on chemical modeling, and not unique to the program PHREEQE.

Experience acquired to date in using PHREEQE to simulate natural water systems has shown that in many cases a reaction, or reaction path, that models a given set of observed chemical changes <u>is not mathematically unique</u>. That is, the observed changes in water chemistry can often be modeled exactly by two or (in most cases) more distinct reactions or reaction paths. Thus, the PHREEQE user really faces two distinct questions: (1) can a model be found that simulates the desired chemical system (natural or laboratory), and (2) if a satisfactory model is found, is it the only model that simulates the system in question? The second question is often as difficult to answer, and as important, as the first.

TEST PROBLEMS*

The test problems that follow are designed to illustrate ways of setting up input decks for a wide range of problems that can be considered by PHREEQE. For each problem, the input data deck is listed with a brief explanation. Printed results from PHREEQE are listed for two test problems (1 and 4) which may be useful for comparison purposes in making PHREEQE operational on other computer systems*. Critical details of the results of all the test problems are summarized and discussed briefly.

Test Problem 1 - Changing the Data Base and Calculating the Distribution of Species in Seawater.

In this first test case we are interested in using PHREEQE as a model to calculate the distribution of species in a seawater sample. The problem is complicated by the fact that the seawater analysis (table 2) contains analytical data for NO_3^-, NH_4^+, and U. The nitrogen system in the preliminary PHREEQE data base has been constructed to calculate NH_4^+ and NO_3^- from total nitrogen, pe, pH and the aqueous model. No thermodynamic data for uranium are included in the PHREEQE preliminary data base. So in addition to solving for the distribution of species in a seawater sample, this test case demonstrates:

1. How to reconstruct the existing data base for a particular element to represent disequilibrium between oxidation states of the element; and

2. How to add a new element (and associated aqueous model) to the existing data base.

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* For this version of the PHREEQE manual, results from test problem #1 were generated using the current FORTRAN 77 version and may be used for comparison purposes. Similar, but not always identical, results will be found for test problems 2 - 5, as these test cases have not been updated in this version of the manual.

Table 2. - Seawater composition [1]

Number	Species of element	Concentration in ppm
4	Ca	412.3
5	Mg	1291.8
6	Na	10768.0
7	K	399.1
8	Fe	0.002
9	Mn	0.0002
10	Al	0.002
11	Ba	0.02
12	Sr	8.14
13	SiO_2	4.28
14	Cl	19353.0
15	Alk (as HCO_3^-)	141.682 [a]
16	SO_4	2712.0
17	NO_3	0.290
18	B	4.45
19	PO_4	0.06
20	F	1.39
21	Li	0.181
22	Br	67.3
23 [b]	NH_4	0.03
24 [b]	U	0.0033

25°C, pH = 8.22, pe = 8.451, density = 1.023

[1] From Nordstrom and others (1979) with uranium added.

[a] Total titration alkalinity as HCO_3^-. Added significant figures for computational purposes only. (See Nordstrom and others, 1979.) Note that ELEMENTS input is required to change the gram formula weight of carbon (as CO_2) to the equivalent weight of the alkalinity species, HCO_3^-.

[b] "ELEMENTS" to be added to the data base. SPECIES input will also be required.

1. Existing nitrogen system in data base.

The nitrogen speciation is calculated from total nitrogen, pe, pH and the aqueous model using NO_3^- as the master species (number 17). Pertinent equilibria are listed in table 3.

Table 3. - Existing nitrogen data base

Species		Reaction	log K	ΔH^o_r
48	NO_2^-	$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$	28.57	-43.76
49	N_2^o	$2NO_3^- + 12H^+ + 10e^- = N_2^o + 6H_2O$	207.08	-312.13
50	NH_3^o	$NO_3^- + 9H^+ + 8e^- = NH_3^o + 3H_2O$	109.83	-174.58
51	NH_4^+	$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$	119.077	-187.055
52	$NH_4SO_4^-$	$NO_3^- + 10H^+ + 8e^- + SO_4^{2-} = NH_4SO_4^- + 3H_2O$	120.19	-187.055
142	$Mn(NO_3)_2^o$	$2NO_3^- + Mn^{2+} = Mn(NO_3)_2^o$	0.6	-0.396

Note that all the nitrogen reactions are written as association from NO_3^- in the existing data base.

2. Reconstructed nitrogen system.

In the reconstructed nitrogen system, total NO_3^- and total NH_4^+ are entered as separate "ELEMENTS". Two master species are used, NO_3^- (number 17) and NH_4^+ (number 23). For purposes of this example, we have <u>arbitrarily</u> chosen to delete N_2^o from the aqueous model and to calculate NO_2^- from NO_3^-. The reconstructed nitrogen equilibria are listed in table 4.

Table 4. - Reconstructed nitrogen data base

Species		Reaction	log K	ΔH^o_r
48	NO_2^-	$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$	28.57	-43.76
49	- - - - - blank card to delete N_2^o - - - - - - - - - - - - - -			
50	NH_3^o	$NH_4^+ = NH_3^o + H^+$	-9.244	12.47
51	- - blank card to delete calculation of NH_4^+ from NO_3^- - - - -			
52	$NH_4SO_4^-$	$NH_4^+ + SO_4^{2-} = NH_4SO_4^-$	1.11	0.0
142	$Mn(NO_3)_2^o$	$2NO_3^- + Mn^{2+} = Mn(NO_3)_2^o$	0.6	-0.396

In the reconstructed data base we now have nitrogen speciation for NH_4^+ and NO_3^- considered separately, with reactions written in terms of the "new" master species, NH_4^+. Although the thermodynamic data listed here are realistic, they have been compiled from various sources and are not documented. These data are given for example purposes only and should be checked before application to specific problems.

3. Adding uranium to the data base.

In order to add a new element to the data base, the thermodynamic data base for the aqueous model of that element must be compiled. This is obviously no simple task and requires a critical evaluation of the existing thermochemical literature for the particular element. The uranium data listed below were compiled by F.J. Pearson, Jr. (personal communication) largely from Langmuir (1978) and Baes and Mesmer (1976), but have not been documented in detail. The aqueous data for uranium are given below for example purposes and may not be complete enough for application to seawater or solutions containing significant amounts of dissolved phosphate and flouride.

In adding uranium to the data base, U^{4+} was chosen as the master species (number 24). The (arbitrarily defined) species numbers, reactions, thermodynamic data for reactions, Debye-Hückel activity coefficient parameters, and estimates of species contributions to total alkalinity, as used in the updated data base are listed in table 5.

Table 5. - Preliminary aqueous data for uranium 1/

	Species	THSP	ALKSP	Reaction	log K	ΔH^o_r
24	U^{4+}	4.0	0.0	$U^{4+} = U^{4+}$	0.0	0.0
188	$U(OH)_4^o$	4.0	0.0	$U^{4+} + 4H_2O = U(OH)_4^o + 4H^+$	-8.538	24.76
189	$U(OH)_5^-$	4.0	1.0	$U^{4+} + 5H_2O = U(OH)_5^- + 5H^+$	-13.147	27.58
190	UO_2^+	5.0	0.0	$U^{4+} + 2H_2O = UO_2^+ + 4H^+ + e^-$	-6.432	31.13
191	UO_2^{2+}	6.0	0.0	$U^{4+} + 2H_2O = UO_2^{2+} + 4H^+ + 2e^-$	-9.217	34.43
192	$(UO_2)_2(OH)_2^{2+}$	12.0	2.0	$2U^{4+} + 6H_2O = UO_2(OH)_2^{2+} + 10H^+ + 4e^-$	-24.060	32.82
193	$(UO_2)_3(OH)_5^+$	18.0	5.0	$3U^{4+} + 11H_2O = (UO_2)_3(OH)_5^+ + 17H^+ + 6e^-$	-43.292	59.02
194	$UO_2CO_3^o$	10.0	2.0	$U^{4+} + 2H_2O + CO_3^{2-} = UO_2CO_3^o + 4H^+ + 2e^-$	0.847	35.27
195	$UO_2(CO_3)_2^{2-}$	14.0	4.0	$U^{4+} + 2H_2O + 2CO_3^{2-} = UO_2(CO_3)_2^{2-} + 4H^+ + 2e^-$	7.760	37.91
196	$UO_2(CO_3)_3^{4-}$	18.0	6.0	$U^{4+} + 2H_2O + 3CO_3^{2-} = UO_2(CO_3)_3^{4-} + 4H^+ + 2e^-$	12.180	25.65
197	UO_2OH^+	6.0	1.0	$U^{4+} + 3H_2O = UO_2OH^+ + 5H^+ + 2e^-$	-14.999	45.445

1/ Compiled by F.J. Pearson, Jr. (personal communication) from various sources but largely Langmuir (1978) and Baes and Mesmer (1976). The Debye-Hückel ion size parameter is not known for these species (values of zero appear in the modified data base).

4. Optional LOOK MIN input

Because NO_3^- and NH_4^+ equilibria are calculated independently, and we have independent analytical data for NO_3^- and NH_4^+, we can use LOOK MIN cards to calculate the apparent pe of the seawater sample as implied by the $NO_3^- - NH_4^+$ couple. The reaction of interest (from the preliminary data base) is

	log K	ΔH^o_r
$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$	119.077	-187.055

The mass action expression is

$$\frac{a_{NH_4^+} \cdot a^3_{H_2O}}{a_{NO_3^-} \cdot a^{10}_{H^+} \cdot a^8_{e^-}} = 10^{119.077} \quad (25^oC) .$$

Taking the logarithum of the mass action expression and solving for pe, we have

$$pe = -\log a_{e^-} = \log K + \log IAP$$

$$\text{where } \log K = \frac{119.077}{8} = 14.885 \text{ , } \Delta H^o_r = \frac{-187.055}{8} = -23.382,$$

and $\log IAP = 0.125 \log a_{NO_3^-} + 1.25 \log a_{H^+} - 0.125 \log a_{NH_4^+} - 0.375 \log a_{H_2O}$. In order to calculate pe for the $NO_3^- - NH_4^+$ couple using LOOK MIN input, we enter the expression

$$\text{PENO3NH4} = 0.125\ NO_3^- + 1.25\ H^+ - 0.125\ NH_4^+ - 0.375\ H_2O .$$

Normally, the data in LOOK MIN are used for calculation of mineral saturation indices where the mineral on the left side of the equilibrium is balanced in charge. In the reaction above, the "mineral" is e^-, and thus the program will print a non-fatal warning that the mineral reaction is not balanced in charge. By changing the sign of log K and ΔH^o_r we can use the log (IAP/K) LOOK MIN calculation to calculate pe for the reaction.

Finally, having introduced uranium chemistry to the data base, we can include LOOK MIN cards for uranium minerals (uraninite in this case) in order to calculate their saturation state in seawater. The uraninite reaction used in this test problem is:

$$UO_2 \text{ (uraninite)} + 4H^+ = U^{4+} + 2H_2O$$

$$\log K = -3.49 \quad , \Delta H^o_r = -18.63 \; .$$

5. Card input data deck

The data set required to solve this particular problem includes 84 cards which are listed in table 6. Note that cards 7, 15, 18, 24 69, and 83 are blank. The card numbers, their type and general function are outlined as follows:

Card Number	Type	Function
1	A.1	Title information for the problem.
2	A.2	Option card - defines the type of calculations to be made and type of input to follow.
3-7	B.1	ELEMENTS input defining the equivalent weight of bicarbonate, and the gram formula weights of new elements U and N as U^{4+} and NH_4^+.
8-16	B.2	SPECIES cards defining NH_4^+ and U^{4+} as master species.
17-28	B.2	SPECIES cards re-defining NH_4^+ speciation.
29-69	B.2	SPECIES cards defining the uranium aqueous model as given in table 5.
70-77	B.3	SOLUTION n cards defining solution 1 (seawater).
78-83	B.5	LOOK MIN cards for calculation of uraninite saturation, and pe from the NO_3^- - NH_4^+ couple.
84	B.11	END. Denotes end of input for this problem.

Table 6. - Card images of input data set for test problem 1

```
CARD NO.                                      COLUMN

            1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

 1  TEST PROBLEM #1  CHANGE DATA BASE AND SPECIATE SEAWATER.
 2  000001000  0 0      0.0
 3  ELEMENTS
 4  C         15    61.0171       HCO3-
 5  NH4       23    18.0386       NH4+
 6  U         24    238.029       U4+
 7
 8  SPECIES
 9   23
10  NH4+        100 1.0       -3.0      2.5                           0.0
11  0.0       0.0
12   23 1.0
13   24
14  U4+         100  +4.0      +4.0     0.0
15
16   24  1.0
17   49
18
19   50
20  NH3 AQ      200 0.0       -3.0      0.0                           1.0
21  -9.244    12.47
22   23 1.0     1 -1.0
23   51
24
25   52
26  NH4SO4-     200 -1.0      3.0       0.0                           0.0
27  1.11      0.0
28   23 1.0    16 1.0
29  188
30  U(OH)4      300   0.0      +4.0      0.0
31   -8.538    24.76
32   24  1.0    3  4.0    1 -4.0
33  189
34  U(OH)5-     300  -1.0      +4.0     0.0                            1.0
35   -13.147   27.58
36   24  1.0    3  5.0    1 -5.0
37  190
38  UO2+        400  +1.0      +5.0      0.0
39   -6.432    31.13
40   24  1.0    3  2.0    1 -4.0    2 -1.0
41  191
42  UL=UO2+2    400  +2.0      +6.0     0.0
43   -9.217    34.43
44   24  1.0    3  2.0    1 -4.0    2 -2.0
45  192
46  UL2OH2+2    400  +2.0     +12.0     0.0                            2.0
47   -24.060   32.82
48   24  2.0    3  6.0    1-10.0    2 -4.0
49  193
50  UL3OH5+     400  +1.0     +18.0     0.0                            5.0

    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
            1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
```

```
CARD NO.                                 COLUMN

              1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

  51  -43.292    59.02
  52   24  3.0    3 11.0    1-17.0    2 -6.0
  53  194
  54  ULCO3       500   0.0     +10.0      0.0                          2.0
  55    0.847     35.27
  56   24  1.0    3  2.0   15  1.0    1 -4.0    2 -2.0
  57  195
  58  ULCO32-2    500 -2.0      +14.0     0.0                           4.0
  59    7.760     37.91
  60   24  1.0    3  2.0   15  2.0    1 -4.0    2 -2.0
  61  196
  62  ULCO33-4    500 -4.0      +18.0      0.0                          6.0
  63    12.180    25.65
  64   24  1.0    3  3.0   15  3.0    1 -4.0    2 -2.0
  65  197
  66  ULOH+       400 +1.0       +6.0     0.0                           1.0
  67   -14.999    45.445
  68   24  1.0    3  3.0    1 -5.0    2 -2.0
  69
  70  SOLUTION 1
  71  SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.
  72  21 15 3   8.22      8.451     25.0      1.023
  73     4 412.3        5 1291.8       6 10768.0      7 399.1        8 0.002
  74     9 0.0002      10 0.002       11 0.02        12 8.14        13 4.28
  75    14 19353.0     15 141.682     16 2712.0      17 0.290       18 4.45
  76    19 0.06        20 1.39        21 0.181       22 67.3        23 0.03
  77    24  .0033
  78  LOOK MIN
  79  URANINIT   3          4.0     -3.49    -18.63    0
  80    24        1.0   3        2.0   1       -4.0
  81  PENO3NH4   4          1.0   -14.885    23.382    0
  82    17      0.125   1       1.25  23     -0.125   3    -0.375
  83
  84  END
```

6. Output for test problem 1

Printed output for test problem 1 are reproduced in table 7. The first two pages of the output list the input data set. The listing of the input data set is performed during the read operation, so that if there are coding errors, the error messages are closely related to the source of the problem. Note that the print format for the input data set may not contain the same number of significant figures as on the input cards. (Card images of the input data set are given in table 6). A warning is printed on the second page of output noting lack of charge balance in LOOK MIN input for PENO3NH4. Normally this message indicates an error in coding LOOK MIN data, but in this special case, as discussed above, there is no error when using LOOK MIN for redox couples. Pages 2-6 of the output list (1) the computed total molalities of the elements in seawater (computed from ppm data), (2) the description of solution including pH, pe, water activity, ionic strength, temperature, charge imbalance (equivalents/kg H_2O), OPV state (THOR) of the solution ($= \sum_i m_i v_i$ for the solution; see Equilibrium Equations), total alkalinity of the solution in equivalents per kg H_2O, and the number of iterations through the aqueous model required to solve the problem, (3) distribution of species which lists the molality, activity, activity coefficient and log values for all species with molalities greater than 10^{-30}, including the newly added uranium species, and (4) LOOK MIN IAP which gives log IAP, log K and saturation index (log IAP/K) for each mineral in the LOOK MIN data for which sufficient chemical data were given to allow their calculation. Note that the new minerals uraninite and PENO3NH4 appear in the list, and in the case of PENO3NH4, pe from the $NO_3^- - NH_4^+$ couple is 4.6743.

Table 7. - Printout from test problem 1

```
          DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
1TEST PROBLEM #1  CHANGE DATA BASE AND SPECIATE SEAWATER.
 0000010000 0 0         0.00000
 ELEMENTS
 C          15        0.61017E+02
 NH4        23        0.18039E+02
 U          24        0.23803E+03
             0        0.00000E+00
 SPECIES
  23
 NH4+        100     1.000    -3.000     2.500     0.000     0.000     0.000
      0.000     0.000 0.00000     0.00000     0.00000     0.00000     0.00000
  23  1.000
  24
 U4+         100     4.000     4.000     0.000     0.000     0.000     0.000
      0.000     0.000 0.00000     0.00000     0.00000     0.00000     0.00000
  24  1.000
  49
             000     0.000     0.000     0.000     0.000     0.000     0.000
  50
 NH3 AQ      200     0.000    -3.000     0.000     0.000     0.000     1.000
     -9.244    12.470 0.00000     0.00000     0.00000     0.00000     0.00000
  23  1.000  1 -1.000
  51
             000     0.000     0.000     0.000     0.000     0.000     0.000
  52
 NH4SO4-     200    -1.000     3.000     0.000     0.000     0.000     0.000
      1.110     0.000 0.00000     0.00000     0.00000     0.00000     0.00000
  23  1.000 16  1.000
 188
 U(OH)4      300     0.000     4.000     0.000     0.000     0.000     0.000
     -8.538    24.760 0.00000     0.00000     0.00000     0.00000     0.00000
  24  1.000  3  4.000  1 -4.000
 189
 U(OH)5-     300    -1.000     4.000     0.000     0.000     0.000     1.000
    -13.147    27.580 0.00000     0.00000     0.00000     0.00000     0.00000
  24  1.000  3  5.000  1 -5.000
 190
 UO2+        400     1.000     5.000     0.000     0.000     0.000     0.000
     -6.432    31.130 0.00000     0.00000     0.00000     0.00000     0.00000
  24  1.000  3  2.000  1 -4.000  2 -1.000
 191
 UL=UO2+2    400     2.000     6.000     0.000     0.000     0.000     0.000
     -9.217    34.430 0.00000     0.00000     0.00000     0.00000     0.00000
  24  1.000  3  2.000  1 -4.000  2 -2.000
 192
 UL2OH2+2    400     2.000    12.000     0.000     0.000     0.000     2.000
    -24.060    32.820 0.00000     0.00000     0.00000     0.00000     0.00000
  24  2.000  3  6.000  1-10.000  2 -4.000
 193
 UL3OH5+     400     1.000    18.000     0.000     0.000     0.000     5.000
    -43.292    59.020 0.00000     0.00000     0.00000     0.00000     0.00000
  24  3.000  3 11.000  1-17.000  2 -6.000
 194
 ULCO3       500     0.000    10.000     0.000     0.000     0.000     2.000
      0.847    35.270 0.00000     0.00000     0.00000     0.00000     0.00000
```

```
 24  1.000  3  2.000 15  1.000  1 -4.000  2 -2.000
195
ULCO32-2     500    -2.000    14.000      0.000      0.000      0.000      4.000
     7.760    37.910 0.00000    0.00000    0.00000    0.00000    0.00000
 24  1.000  3  2.000 15  2.000  1 -4.000  2 -2.000
196
ULCO33-4     500    -4.000    18.000      0.000      0.000      0.000      6.000
    12.180    25.650 0.00000    0.00000    0.00000    0.00000    0.00000
 24  1.000  3  2.000 15  3.000  1 -4.000  2 -2.000
197
ULOH+        400     1.000     6.000      0.000      0.000      0.000      1.000
   -14.999    45.445 0.00000    0.00000    0.00000    0.00000    0.00000
 24  1.000  3  3.000  1 -5.000  2 -2.000
  0
SOLUTION 1
SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.
21 15 3     8.22       8.45       25.0       1.02
   4  4.123D+02   5  1.292D+03   6  1.077D+04   7  3.991D+02   8  2.000D-03
   9  2.000D-04  10  2.000D-03  11  2.000D-02  12  8.140D+00  13  4.280D+00
  14  1.935D+04  15  1.417D+02  16  2.712D+03  17  2.900D-01  18  4.450D+00
  19  6.000D-02  20  1.390D+00  21  1.810D-01  22  6.730D+01  23  3.000D-02
  24  3.300D-03
LOOK MIN
URANINIT   3               -3.49     -18.6         0
  24   1.00        3   2.00        1  -4.00
PENO3NH4   4               -14.9      23.4         0
  17  0.125        1   1.25       23 -0.125        3 -0.375
          0             0.000     0.000           0
***** WARNING:  LOOK MINERAL NUMBER  28  PENO3NH4 REACTION
      DOES NOT CHARGE BALANCE.
1SOLUTION NUMBER 1
 SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.


                         TOTAL MOLALITIES OF ELEMENTS
                         ----- ---------- -- --------

               ELEMENT          MOLALITY           LOG MOLALITY

               CA              1.066184D-02          -1.9722
               MG              5.508663D-02          -1.2590
               NA              4.854521D-01          -0.3139
               K               1.057963D-02          -1.9755
               FE              3.711732D-08          -7.4304
               MN              3.773146D-09          -8.4233
               AL              7.682639D-08          -7.1145
               BA              1.509423D-07          -6.8212
               SR              9.628700D-05          -4.0164
               SI              7.382939D-05          -4.1318
               CL              5.657725D-01          -0.2474
               TOT ALK         2.406632D-03          -2.6186
               S               2.926130D-02          -1.5337
               N               4.847508D-06          -5.3145
               B               4.266589D-04          -3.3699
               P               6.547944D-07          -6.1839
               F               7.583056D-05          -4.1202
               LI              2.702732D-05          -4.5682
               BR              8.729574D-04          -3.0590
```

```
NH4            1.723713D-06          -5.7635
U              1.436913D-08          -7.8426



                ----DESCRIPTION OF SOLUTION----

                              PH =   8.2200
                              PE =   8.4510
                  ACTIVITY H2O =   0.9805
                IONIC STRENGTH =   0.6799
                   TEMPERATURE =  25.0000
            ELECTRICAL BALANCE =   9.4423D-05
                          THOR =   1.8412D-01
              TOTAL ALKALINITY =   2.4066D-03
                    ITERATIONS =  14
                  TOTAL CARBON =   2.1343D-03


                     ----------------------
                     DISTRIBUTION OF SPECIES
                     ----------------------

 I  SPECIES     Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 1 H+         1.0  8.066E-09   -8.093   6.026E-09  -8.220  7.470E-01  -0.127
 2 E-        -1.0  3.540E-09   -8.451   3.540E-09  -8.451  1.000E+00   0.000
 3 H2O        0.0  9.805E-01   -0.009   9.805E-01  -0.009  1.000E+00   0.000
 4 CA+2       2.0  9.438E-03   -2.025   2.353E-03  -2.628  2.493E-01  -0.603
 5 MG+2       2.0  4.874E-02   -1.312   1.404E-02  -1.853  2.880E-01  -0.541
 6 NA+        1.0  4.788E-01   -0.320   3.381E-01  -0.471  7.061E-01  -0.151
 7 K+         1.0  1.041E-02   -1.983   6.476E-03  -2.189  6.223E-01  -0.206
 8 FE+2       2.0  1.119E-14  -13.951   3.484E-15 -14.458  3.114E-01  -0.507
 9 MN+2       2.0  2.114E-09   -8.675   6.583E-10  -9.182  3.114E-01  -0.507
10 AL+3       3.0  1.087E-16  -15.964   7.874E-18 -17.104  7.244E-02  -1.140
11 BA+2       2.0  1.509E-07   -6.821   4.700E-08  -7.328  3.114E-01  -0.507
12 SR+2       2.0  7.930E-05   -4.101   1.936E-05  -4.713  2.441E-01  -0.612
13 H4SIO4     0.0  7.164E-05   -4.145   8.378E-05  -4.077  1.169E+00   0.068
14 CL-       -1.0  5.658E-01   -0.247   3.521E-01  -0.453  6.223E-01  -0.206
15 CO3-2     -2.0  3.748E-05   -4.426   7.759E-06  -5.110  2.070E-01  -0.684
16 SO4-2     -2.0  1.554E-02   -1.808   2.811E-03  -2.551  1.808E-01  -0.743
17 NO3-      -1.0  4.847E-06   -5.314   3.621E-06  -5.441  7.470E-01  -0.127
18 H3BO3      0.0  3.712E-04   -3.430   4.341E-04  -3.362  1.169E+00   0.068
19 PO4-3     -3.0  3.308E-11  -10.480   2.396E-12 -11.620  7.244E-02  -1.140
20 F-        -1.0  3.893E-05   -4.410   2.908E-05  -4.536  7.470E-01  -0.127
21 LI+        1.0  2.670E-05   -4.573   1.995E-05  -4.700  7.470E-01  -0.127
22 BR-       -1.0  8.730E-04   -3.059   6.521E-04  -3.186  7.470E-01  -0.127
23 NH4+       1.0  1.572E-06   -5.804   1.174E-06  -5.930  7.470E-01  -0.127
24 U4+        4.0  3.041E-55  -54.517   2.859E-57 -56.544  9.403E-03  -2.027
31 OH-       -1.0  2.188E-06   -5.660   1.635E-06  -5.787  7.470E-01  -0.127
32 O2 AQ      0.0  3.303E-20  -19.481   3.863E-20 -19.413  1.169E+00   0.068
34 HCO3-     -1.0  1.478E-03   -2.830   9.969E-04  -3.001  6.745E-01  -0.171
50 NH3 AQ     0.0  9.500E-08   -7.022   1.111E-07  -6.954  1.169E+00   0.068
52 NH4SO4-   -1.0  5.692E-08   -7.245   4.252E-08  -7.371  7.470E-01  -0.127
57 H2BO3-    -1.0  5.549E-05   -4.256   4.145E-05  -4.382  7.470E-01  -0.127
65 HPO4-2    -2.0  1.029E-07   -6.988   3.203E-08  -7.494  3.114E-01   0.507
76 CACO3      0.0  2.622E-05   -4.581   3.067E-05  -4.513  1.169E+00   0.068
```

```
 77 CAHCO3+   1.0  4.437E-05   -4.353   2.993E-05  -4.524  6.745E-01  -0.171
 78 CASO4     0.0  1.152E-03   -2.939   1.347E-03  -2.871  1.169E+00   0.068
 79 CAPO4-   -1.0  2.172E-08   -7.663   1.622E-08  -7.790  7.470E-01  -0.127
 80 CAHPO4    0.0  3.533E-08   -7.452   4.131E-08  -7.384  1.169E+00   0.068
 82 CAF+      1.0  7.977E-07   -6.098   5.959E-07  -6.225  7.470E-01  -0.127
 86 MGCO3     0.0  8.916E-05   -4.050   1.043E-04  -3.982  1.169E+00   0.068
 87 MGHCO3+   1.0  2.192E-04   -3.659   1.637E-04  -3.786  7.470E-01  -0.127
 88 MGSO4     0.0  6.000E-03   -2.222   7.017E-03  -2.154  1.169E+00   0.068
 89 MGPO4-   -1.0  1.748E-07   -6.758   1.306E-07  -6.884  7.470E-01  -0.127
 90 MGHPO4    0.0  2.850E-07   -6.545   3.333E-07  -6.477  1.169E+00   0.068
 92 MGF+      1.0  3.610E-05   -4.442   2.697E-05  -4.569  7.470E-01  -0.127
 95 NACO3-   -1.0  6.509E-05   -4.186   4.863E-05  -4.313  7.470E-01  -0.127
 96 NAHCO3    0.0  1.625E-04   -3.789   1.900E-04  -3.721  1.169E+00   0.068
 97 NASO4-   -1.0  6.377E-03   -2.195   4.763E-03  -2.322  7.470E-01  -0.127
 98 NAHPO4-  -1.0  2.827E-08   -7.549   2.111E-08  -7.675  7.470E-01  -0.127
100 KSO4-    -1.0  1.725E-04   -3.763   1.289E-04  -3.890  7.470E-01  -0.127
115 FE+3      3.0  1.262E-18  -17.899   9.143E-20 -19.039  7.244E-02  -1.140
117 FEOH2+    1.0  6.961E-09   -8.157   5.200E-09  -8.284  7.470E-01  -0.127
118 FEOH3     0.0  8.501E-09   -8.071   9.941E-09  -8.003  1.169E+00   0.068
119 FEOH4-   -1.0  2.166E-08   -7.664   1.618E-08  -7.791  7.470E-01  -0.127
137 MNCL+     1.0  1.255E-09   -8.901   9.377E-10  -9.028  7.470E-01  -0.127
138 MNCL2     0.0  7.669E-11  -10.115   8.968E-11 -10.047  1.169E+00   0.068
141 MNSO4     0.0  2.879E-10   -9.541   3.367E-10  -9.473  1.169E+00   0.068
152 ALOH3     0.0  2.901E-09   -8.537   3.393E-09  -8.469  1.169E+00   0.068
153 ALOH4-   -1.0  7.390E-08   -7.131   5.521E-08  -7.258  7.470E-01  -0.127
168 SRSO4     0.0  1.651E-05   -4.782   1.931E-05  -4.714  1.169E+00   0.068
170 H3SIO4-  -1.0  2.192E-06   -5.659   1.637E-06  -5.786  7.470E-01  -0.127
181 LISO4-   -1.0  3.276E-07   -6.485   2.447E-07  -6.611  7.470E-01  -0.127
195 ULCO32-2 -2.0  1.851E-09   -8.733   5.764E-10  -9.239  3.114E-01  -0.507
196 ULCO33-4 -4.0  1.251E-08   -7.903   1.176E-10  -9.929  9.403E-03  -2.027
```

```
                  ---- LOOK MIN IAP ----

      PHASE         LOG IAP      LOG KT      LOG IAP/KT

     CALCITE        -7.7386      -8.4798       0.7412
     ARAGONIT       -7.7386      -8.3361       0.5974
     DOLOMITE      -14.7015     -17.0900       2.3885
     SIDERITE      -19.5681     -10.5700      -8.9981
     RHODOCHR      -14.2918     -10.4100      -3.8818
     STRONTIT       -9.8234      -9.2705      -0.5528
     GYPSUM         -5.1966      -4.6028      -0.5939
     ANHYDRIT       -5.1796      -4.3840      -0.7956
     CELESTIT       -7.2643      -6.5780      -0.6863
     BARITE         -9.8790      -9.9780       0.0990
     HYDROXAP       -2.7541      -3.4210       0.6669
     FLUORITE      -11.7013     -10.9600      -0.7413
     CHALCEDY       -4.0598      -3.5230      -0.5368
     QUARTZ         -4.0598      -4.0060      -0.0538
     GIBBSITE        7.5305       8.7700      -1.2395
     KAOLINIT      -39.0500     -36.9210      -2.1290
     SEPIOLIT      -39.0438     -40.0790       1.0352
     HEMATITE       11.2165      -4.0080      15.2245
     GOETHITE        5.6040       0.4860       5.1180
     FEOH3A          5.5954       4.8910       0.7044
     PYRITE       -202.0218     -18.4800    -183.5418
     FES PPT      -116.6909      -3.9150    -112.7759
     VIVIANIT      -66.6831     -36.0000     -30.6831
     PCO2           -4.8609      -1.4679      -3.3930
```

O2 GAS	-19.4131	-2.9600	-16.4531
H2 GAS	-36.4920	-3.1500	-33.3420
URANINIT	-23.6809	-3.4900	-20.1909
PENO3NH4	-10.2107	-14.8850	4.6743

(BLANK PAGE)

Test Problem 2 - Mixing Zone Dolomitization

The second problem uses PHREEQE to investigate carbonate diagenetic reactions that may occur in mixing zones between fresh carbonate groundwater and seawater. Specifically we ask the following questions: (1) what are the saturation indices of calcite and dolomite in a closed system mixture containing 30 percent seawater and 70 percent limestone groundwater, (2) what are the mass transfers of calcite and dolomite (per kg H_2O) if the closed system mixture equilibrates with calcite and dolomite, and (3) what is the mass transfer if the closed system mixture (for kinetic reasons) equilibrates with calcite but not with dolomite?

To solve this problem we first need to define two solutions: (1) a limestone groundwater (for this problem we arbitrarily choose a water in equilibrium with calcite at $10^{-2.0}$ atm P_{CO_2}), and (2) seawater. All calculations are at 25°C.

Table 8 lists the input data set (47 cards) used to solve problem 2. The problem has been divided into 4 parts, A, B, C, and D.

Part A (cards 1-13) constructs the limestone groundwater by equilibrating pure water with calcite at $10^{-2.0}$ atm P_{CO_2} and 25°C. The problem is defined by the option card (card 2) which determines that:

1. The pH of the initial solution (pure water) will be adjusted to obtain charge balance (IOPT(2) = 1, we could also have used IOPT(2) = 0).
2. The problem is one of equilibrating a starting solution with minerals (IOPT(3) = 5).
3. The calculation is at constant temperature (IOPT(4) = 0).
4. pe is to be held constant because this is not a redox problem (IOPT(5) = 0). The calculation could also be made with IOPT(5) equal to 1, but more computation time would be required in calculation of pe (which has little meaning in this problem).
5. Activity coefficients are calculated using the Davies equation (IOPT(6) = 1).
6. The solution calculated at the end of part A (the limestone groundwater) is saved under Solution 1 for future use in the simulation (IOPT(7) = 1).

Table 8. - Card images of input data set for test problem 2.

```
CARD NO.                               COLUMN

             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

  1   TEST PROBLEM #2 PART A - CALCITE EQUILIBRIUM AT LOG PCO2 = -2.0 AND 25C.
  2   015001100  0 0             0.0
  3   SOLUTION 1
  4   PURE WATER
  5    0  0 0          7.0       4.0      25.0       1.0
  6   MINERALS
  7   FIX PCO2   2      4.0     -1.466    -4.708        0               -2.0
  8     35  1.0         3 -1.0
  9   CALCITE    2   4.0       -8.47     -2.58          1
 10     15 1.0          4 1.0
 11   13.543      -0.0401     -3000.0
 12
 13   END
 14   TEST PROBLEM #2 PART B - CLOSED SYSTEM MIXTURE OF PREVIOUS SOLN WITH SEAWATER
 15   021001100  1 0             0.0
 16   ELEMENTS
 17   C         15      61.0171
 18   SI        13      96.1147
 19
 20   SOLUTION 2
 21   SEA WATER
 22   10 15 3         8.22     8.451      25.0     1.023
 23      4      412.3   5     1291.8   6     10768.   7      399.1  14     19353.
 24     16      2712.  12        8.1  13       6.85  18        4.5  15      141.7
 25   STEPS
 26          0.7
 27   NEUTRAL
 28       6   14
 29   END
 30   TEST PROBLEM #2 PART C - EQUILIBRATE MIXTURE WITH CALCITE AND DOLOMITE.
 31   005001000  0 0             0.0
 32   MINERALS
 33   CALCITE    2   4.0       -8.47     -2.58          1
 34     15 1.0          4 1.0
 35   13.543      -0.0401     -3000.0
 36   DOLOMITE   3   8.0       -17.020   -8.29          0
 37      4 1.0          5 1.0         15 2.0
 38
 39   END
 40   TEST PROBLEM #2 PART D - EQUILIBRATE MIXTURE WITH CALCITE ONLY.
 41   005001000  0 0             0.0
 42   MINERALS
 43   CALCITE    2   4.0       -8.47     -2.58          1
 44     15 1.0          4 1.0
 45   13.543      -0.0401     -3000.0
 46
 47   END
```

Cards 3-5 define pure water as the starting solution 1 and cards 6-12 define the MINERALS (phase boundaries) with which the starting solution will be equilibrated. Card 13 denotes the end of input for Part A.

Part B defines solution 2 (seawater), includes an example of the use of ELEMENTS input for changing gram formula weights for input of analytical data, uses NEUTRAL input to charge balance the starting solution, and makes one closed system mixture of 70 percent solution 1 (groundwater) and 30 percent solution 2 (seawater). The problem is defined by the option card (card 15), and by keyword input in ELEMENTS, SOLUTION, STEPS, and NEUTRAL. Comments are as follows:

1. The totals of one of the elements in the starting solution are to be adjusted to obtain a charge balanced seawater rather than alter the reported pH (IOPT(2) = 2). NEUTRAL input is included (cards 27, 28) to define that either Na or Cl are to be added to obtain charge balance.

2. The problem is one of mixing solution 1 with solution 2 (IOPT(3) = 1). There will be one mixture (NSTEPS on card 15, column 12 is 1) and the fraction of solution 1 in the mixture is 0.7 (STEPS input, cards 25-26).

3. The calculations are isothermal (IOPT(4) = 0), pe is to remain constant (IOPT(5) = 0), activity coefficients are calculated using the Davies equation (IOPT(6) = 1), and the final solution - the solved closed system mixture - is to be retained in solution 1 at the end of part B (IOPT(7) = 1).

4. Cards 16-19 use ELEMENTS input to change the gram formula weight of the silica analytical data from SiO_2 to H_4SiO_4, and carbon to equivalent weight of HCO_3^- because total titration alkalinity as HCO_3^- is entered.

5. Cards 20-24 define the totals of the major elements in seawater entered in SOLUTION 2 (taken from table 2). The last card of part B is END (card 29).

Part C (cards 30-39) equilibrates the closed system mixture (saved at the end of part B) with calcite and dolomite. The problem is defined with the option card (card 31) and other keyword input as follows:

1. pH of the starting solution is not adjusted for charge balance, because the charge balanced solution and pH were determined at the end of part B (IOPT(2) = 0).

2. The problem is one of equilibrating solution 1 with minerals (IOPT(3) = 5).

3. The remaining options are as before except that IOPT(7) = 0 so that solution 1 (saved at the end of part B) will not be changed at the end of part C. Thus the closed system mixture (saved at the end of part B) can be used again in part D.

4. Cards 32-38 of part C define the MINERALS calcite and dolomite for equilibration with the closed system mixture, and card 39 denotes the END of input for part C.

Part D (cards 40-47) is identical to part C except only one MINERAL (calcite) is equilibrated with the closed system mixture saved from part B.

The results of test problem 2 are summarized in table 9, which shows that the closed system mixture is undersaturated with calcite and oversaturated with dolomite (part B). It is interesting to note that the thermodynamics of the system indicate that rather large amounts of calcite should dissolve accompanying the formation of dolomite (part C), but if dolomite fails to precipitate from the mixture, very little mass transfer can actually occur (part D).

Table 9. - Selected results from test problem 2 [a]

Simulation	Number of iterations	pH	log P_{CO_2}	Saturation Index [1] SI_C	SI_D	Mass Transfer, mmols/kg H_2O [2] CO_2	Calcite	Dolomite
Part A [3]	17	7.2965	-2.0	0.0	-	1.983857	1.650955	0.0
Part B [4]	10	7.3704	-2.2505	-0.0928	0.4952	0.0	0.0	0.0
Part C	11	7.0796	-2.0012	0.0	0.0	0.0	14.58147	-7.368827
Part D	11	7.4517	-2.3236	0.0	0.6773	0.0	0.03495	0.0

[a] Results are tabulated for the final solution at the end of each part of the simulation. Additional significant figures are shown for comparison purposes.

[1] Subscripts: C = calcite, D = dolomite.

[2] Positive sign indicates dissolved, negative sign indicates precipitated.

[3] pH of pure water was found to be 6.9990 in 5 iterations.

[4] Seawater was balanced on chloride with 1.018×10^{-3} moles added per kg H_2O. 15 iterations were required. Other parameters of interest for solution 2 (seawater) are: $a_{H_2O} = 0.9805$; ionic strength = 0.6800; total carbon is 2.1375×10^{-3} moles/kg H_2O; $\log P_{CO_2} = -3.3827$; $SI_C = 0.7408$; $SI_D = 2.3270$.

Test Problem 3. - Pyrite Oxidation

This problem investigates the irreversible reaction of oxygen with pyrite. pH is buffered by equilibrium with calcite, and total iron in solution is controlled by goethite equilibrium. Solution composition, pH, pe and mass transfer are calculated for 0.0, 1.0, 5.0, 10.0, and 50.0 net mmols of oxygen added per kg H_2O.

The input data set (19 cards) to solve problem 3 is listed in table 10. The calculations to be made are again defined by the option card (card 2) and keyword input:

1. The starting solution is pure water (cards 3-5) and the pH is adjusted for charge balance (IOPT(2) = 1).
2. A net stoichiometric reaction is added in specified reaction steps (IOPT(3) = 3). There are 5 reaction steps (NSTEP = 5; column 12 of card 2). There is one component in the reaction (O_2) (NCOMPS = 1; column 14, card 2).
3. The reaction is isothermal at the temperature of solution 1 (IOPT(4) =0).
4. pe is to be calculated as a function of reaction (IOPT(5) = 1).
5. The Davies equation is used for individual ion activity coefficients of charged species (IOPT(6) = 1).
6. There is no need to save the final solution at the end of this problem (IOPT(7) = 0).
7. The stoichiometry of the reaction is defined by REACTION input (cards 17-18), and the net moles of the reaction are defined for each step using STEPS input (cards 15-16).
8. Equilibrium with pyrite, goethite, and calcite is stipulated with MINERALS input (cards 6-14).
9. Note that by adding 0.0 moles of oxygen (the first of the 5 reaction steps in STEPS input) we find the equilibrium composition of the closed system. Mass transfer is calculated from solution 1 (pure water) for each reaction step, so there is no significance to the sequence chosen for moles of oxygen added (STEPS input).

Table 10. - Card images of input data set for test problem 3.

```
CARD NO.                               COLUMN

            1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

 1   TEST PROBLEM #3  ADD OXYGEN TO PYRITE-CALCITE-GOETHITE EQUILIBRIUM.
 2   013011000  5 1             0.0
 3   SOLUTION 1
 4   PURE WATER
 5    0  0 0          7.0       4.0      25.0       1.0
 6   MINERALS
 7   PYRITE     4      0.0    -18.48     11.3         0
 8      1  -2.0        2  -2.0        8  1.0        42  2.0
 9   GOETHITE   3   3.0        0.5      -14.48        0
10    115 1.0          3 2.0          1 -3.0
11   CALCITE    2   4.0       -8.47     -2.58         1
12     15 1.0          4 1.0
13   13.543      -0.0401     -3000.0
14
15   STEPS
16          0.0     0.001     0.005      0.01      0.05
17   REACTION
18     32     1.0     4.0
19   END
```

Detailed results of test problem 3 are summarized in table 11. Notice that the final solution is oversaturated with gypsum. A more realistic simulation of the final reaction step would include precipitation of gypsum once the solution becomes supersaturated with gypsum. The amount of oxygen added to the system to reach the gypsum phase boundary can be found by using IOPT(3) = 6, an option used extensively in problem 5.

Table 11. - Selected Results of Test Problem 3 [a]

O_2 [1] added, mmol	Number of iterations	pH	pe	Log P_{CO_2}	Mass Transfer, mmol/kg H_2O pyrite	goethite	calcite	Saturation index gypsum
0.0	35	9.9102	-6.9051	-6.1803	0.000041	-0.000039	0.1226806	-6.4197
1.0	14	7.9907	-3.9581	-3.1942	0.2666971	-0.2662387	1.055461	-1.6997
5.0	15	6.9649	-2.5865	-1.6382	1.335380	-1.304672	4.502924	-0.6626
10.0	16	6.6325	-2.1362	-1.1456	2.675243	-2.546601	8.018004	-0.2710
50.0	17	6.0084	-1.2817	-0.2504	13.48265	-11.24284	30.61820	+0.5592

[a] Net mass transfer from pure water as a function of irreversible addition of oxygen. Starting pe of pure water was arbitrarily chosen as 4.0. Positive delta phase indicates dissolution and negative values indicate precipitation.

[1] O_2 is added irreversibly. Response of pyrite, goethite and calcite is assumed reversible.

Test Problem 4. - Dedolomitization with Sulfate Reduction and Pyrite Formation as a Function of Temperature.

This test problem is designed to investigate some possible reaction paths in limestone-dolostone aquifers that contain trace amounts of gypsum (or anhydrite), organic matter (CH_2O, i.e., carbon of valence zero), pyrite and goethite. The problem is in 5 parts. The first part (A) is used to generate a hypothetical limestone groundwater in equilibrium with calcite and dolomite at 25°C and $10^{-2.0}$ atm P_{CO_2}. This starting solution is saved in solution 1 and subjected to 4 increasingly complex reaction problems (parts B-E) involving various aspects of dedolomitization (dissolution of dolomite and precipitation of calcite driven by irreversible dissolution of calcium sulfate). In each of parts B-E we assume that equilibrium with calcite and dolomite accompanies the irreversible dissolution of 8.0 mmols of gypsum per kg H_2O. Reaction B is the isothermal dedolomitization reaction at 25°C. In this case 8.0 mmols of gypsum are added to solution 1 (saved from part A) while maintaining equilibrium with calcite and dolomite. The mass transfer and solution composition are solved at 4 increments of gypsum dissolution. Reaction C is similar to reaction B but with an added linear temperature change (25-65°C) accompanying the irreversible dissolution of 8.0 mmols of gypsum. The third reaction (D) builds on reaction C by adding a second irreversible reaction - the addition of 4.0 mmols of organic matter (CH_2O) per kg H_2O. The net reaction simulated by addition of organic matter, carbon at valence zero, to the aqueous phase is carbon oxidation via sulfate reduction. It should be emphasized that this is a computed result; the sulfate reduction reaction is not introduced directly via REACTION input. The last reaction (E) includes goethite and pyrite equilibrium with reaction D.

By contrasting the results of reactions B-E, it is possible to observe some of the effects of increased temperature, sulfate reduction, and sulfide precipitation on the dedolomitization reaction. The reaction paths to each final water are generated by solving the net reaction in 4 steps. When more than one irreversible reaction (such as dissolution of gypsum, and oxidation of organic matter) and/or irreversible processes such as changes in temperature occur simultaneously, the calculated reaction path depends on the relative rates of the irreversible reactions and processes. For purposes of these calculations, it is assumed that the relative rates of gypsum dissolution, organic matter oxidation, and temperature change are constant along the reaction path. PHREEQE could be used to examine other reaction paths for the same net reaction by varying the relative rates of reaction with STEPS input and the relative rate of temperature change with TEMPS input. The various options included in the calculations of parts A-E are reviewed as follows (table 12):

Table 12. - Reactions included in test problem 4

Reaction Characteristics	Part				
	A	B	C	D	E
Calcite Equilibrium	X	X	X	X	X
Dolomite Equilibrium	X	X	X	X	X
Dissolve 8 mmol $CaSO_4$		X	X	X	X
Increase T to 65°C			X	X	X
Addition of 4.0 mmol CH_2O				X	X
Goethite and pyrite Equilibrium					X

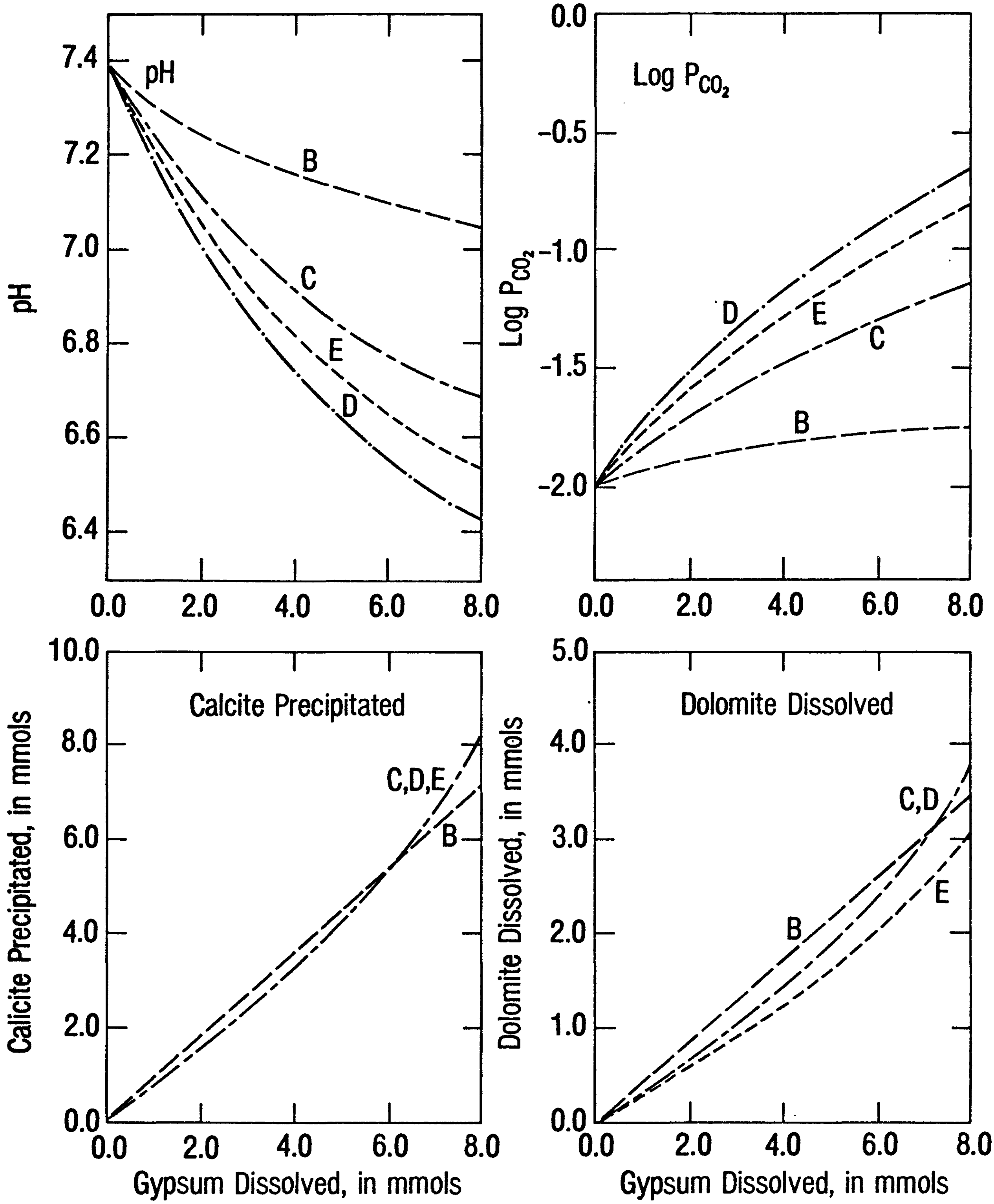
Input data cards to solve parts A-E (81 cards) are listed in table 13. Selected results of parts B-E are summarized in figure 1. All four cases of dedolomitization show decreases in pH and increases in P_{CO2} as gypsum dissolves. The number of moles of dolomite dissolved is approximately half the moles of calcite precipitated as a function of reaction progress. Temperatures above 55°C begin to influence the mass transfer significantly. While differences in the mass transfer of calcite and dolomite are not particularly sensitive to choice of reaction, there are differences in pH and P_{CO2} depending on reaction details. The greatest changes in pH and P_{CO2} accompany reaction D.

Table 13. - Card images of input data set for test problem 4 (parts A-E).

```
CARD NO.                                     COLUMN

              1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

  1   TEST PROBLEM #4 PART A. CALCITE-DOLOMITE EQUILIBRIUM, LPCO2=-2.0, 25C.
  2   015001100  0 0             0.0
  3   SOLUTION 1
  4   PURE WATER
  5    0  0 0         7.0        4.0      25.0       1.0
  6   MINERALS
  7   FIX PCO2   2      4.0     -1.466    -4.708        0              -2.0
  8     35  1.0         3 -1.0
  9   CALCITE    2   4.0       -8.47     -2.58          1
 10     15 1.0          4 1.0
 11   13.543      -0.0401     -3000.0
 12   DOLOMITE   3   8.0       -17.020   -8.29          0
 13      4 1.0          5 1.0         15 2.0
 14
 15   END
 16   TEST PROBLEM #4 PART B - ISOTHERMAL DE-DOLOMITIZATION.
 17   004011000  4 2             0.0
 18   MINERALS
 19   DOLOMITE   3   8.0       -17.020   -8.29          0
 20      4 1.0          5 1.0         15 2.0
 21   CALCITE    2   4.0       -8.47     -2.58          1
 22     15 1.0          4 1.0
 23   13.543      -0.0401     -3000.0
 24
 25   REACTION
 26      4     1.0     0.0  16     1.0     6.0
 27   STEPS
 28        0.008
 29   END
 30   TEST PROBLEM #4 PART C - DE-DOLOMITIZATION WITH INCREASING TEMPERATURE.
 31   004211000  4 2             0.0
 32   MINERALS
 33   CALCITE    2   4.0       -8.47     -2.58          1
 34     15 1.0          4 1.0
 35   13.543      -0.0401     -3000.0
 36   DOLOMITE   3   8.0       -17.020   -8.29          0
 37      4 1.0          5 1.0         15 2.0
 38
 39   REACTION
 40      4     1.0     0.0  16     1.0     6.0
 41   STEPS
 42        0.008
 43   TEMP
 44         25.0      65.0
 45   END
 46   TEST PROBLEM #4 PART D - DE-DOLOMITIZATION,DELTA T,SULFATE REDUCTION.
 47   004211000  4 3             0.0
 48   MINERALS
 49   CALCITE    2   4.0       -8.47     -2.58          1
 50     15 1.0          4 1.0

      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
              1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
```

```
CARD NO.                                    COLUMN

           1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

51  13.543      -0.0401     -3000.0
52  DOLOMITE   3   8.0       -17.020   -8.29          0
53     4 1.0          5 1.0         15 2.0
54
55  REACTION
56     4     1.0     0.0  16     1.0     6.0  15     0.5     0.0
57  STEPS
58       0.008
59  TEMP
60        25.0      65.0
61  END
62  TEST PROBLEM #4 PART E - DE-DOLOMITIZATION,DELTA T,SULFATE REDUCTION,FE PRESENT.
63  004211000  4 3             0.0
64  MINERALS
65  CALCITE    2   4.0       -8.47     -2.58          1
66    15 1.0          4 1.0
67  13.543      -0.0401     -3000.0
68  DOLOMITE   3   8.0       -17.020   -8.29          0
69     4 1.0          5 1.0         15 2.0
70  PYRITE     4      0.0    -18.48     11.3          0
71     1  -2.0        2  -2.0        8  1.0        42  2.0
72  GOETHITE   3   3.0        0.5      -14.48         0
73   115 1.0          3 2.0          1 -3.0
74
75  REACTION
76     4     1.0     0.0  16     1.0     6.0  15     0.5     0.0
77  STEPS
78       0.008
79  TEMP
80        25.0      65.0
81  END
```

Figure 1. - Selected results from test problem 4 (parts B-E) as a function of $CaSO_4$ dissolution.


pH
7.4
7.2
7.0
6.8
6.6
6.4
pH
B
C
E
D
0.0
2.0
4.0
6.0
8.0
Log P_{CO_2}
0.0
-0.5
-1.0
-1.5
-2.0
Log P_{CO_2}
D
E
C
B
0.0
2.0
4.0
6.0
8.0
Calcite Precipitated, in mmols
10.0
8.0
6.0
4.0
2.0
0.0
Calcite Precipitated
C,D,E
B
0.0
2.0
4.0
6.0
8.0
Gypsum Dissolved, in mmols
Dolomite Dissolved, in mmols
5.0
4.0
3.0
2.0
1.0
0.0
Dolomite Dissolved
C,D
B
E
0.0
2.0
4.0
6.0
8.0
Gypsum Dissolved, in mmols

For testing purposes we have solved parts A and E of test problem 4 separately. The input data set to solve the problem is given in table 14 and the resulting output is listed in table 15. The output of table 15 is summarized as follows:

Page	Contents
95	PHREEQE listing of input data set to part A
95	Description of the initial solution (pure water).
96	Results of part A: solution in equilibrium with calcite-dolomite at 25°C and 10^{-2} atm CO_2. Mass transfer from pure water appears as "DELTA PHASE" under "PHASE BOUNDARIES" in units of moles per kg H_2O. Saturation indices appear under "LOOK MIN IAP". The remaining output gives the total molalities of the elements, a description of the solution, and distribution of species.
97	Input data set for part E.
98	Results of the first step in the reaction. Because NSTEPS is 4, the first step in reaction adds 1/4 of the net reaction (defined by reaction input) to solution 1 (defined in part A). Because XSTEP is 0.008 moles, the first step then adds 0.002 moles of the net reaction to solution. The net reaction and new temperature are printed for reference purposes. The total molalities of the elements in solution after the reaction step, but before calculation of the mass transfer needed to achieve phase boundary equilibrium, are listed next. The mass transfer required to equilibrate the solution with the defined MINERALS is listed under "PHASE BOUNDARIES". Appropriate saturation indices from the LOOK MIN data base are given under "LOOK MIN IAP". The total molality of the elements, description of solution, and distribution of species at the end of step 1 follow.

Page	Contents (cont'd.)
100	Similar to pages 97-100, but for step 2 in which 0.004 moles of reaction are added to solution 1 of part A.
103	Similar to pages 97-100, but for step 3 in which 0.006 moles of reaction are added to solution 1 of part A.
105	Similar to pages 97-100, but for step 4 in which 0.008 moles of reaction are added to solution 1 of part A.

Table 14. - Card images of input data set for test problem 4 (parts A and E).

```
CARD NO.                                      COLUMN

            1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

 1  TEST PROBLEM #4 PART A. CALCITE-DOLOMITE EQUILIBRIUM, LPCO2=-2.0, 25C.
 2  015001100  0 0             0.0
 3  SOLUTION 1
 4  PURE WATER
 5   0  0 0         7.0        4.0      25.0       1.0
 6  MINERALS
 7  FIX PCO2   2      4.0     -1.466    -4.708        0              -2.0
 8    35  1.0         3 -1.0
 9  CALCITE    2   4.0       -8.47     -2.58          1
10    15 1.0          4 1.0
11  13.543      -0.0401     -3000.0
12  DOLOMITE   3   8.0       -17.020   -8.29          0
13     4 1.0          5 1.0         15 2.0
14
15  END
16  TEST PROBLEM #4 PART E - DE-DOLOMITIZATION,DELTA T,SULFATE REDUCTION,FE PRESENT.
17  004211000  4 3             0.0
18  MINERALS
19  CALCITE    2   4.0       -8.47     -2.58          1
20    15 1.0          4 1.0
21  13.543      -0.0401     -3000.0
22  DOLOMITE   3   8.0       -17.020   -8.29          0
23     4 1.0          5 1.0         15 2.0
24  PYRITE     4      0.0    -18.48     11.3          0
25     1  -2.0        2  -2.0        8  1.0        42  2.0
26  GOETHITE   3   3.0        0.5      -14.48         0
27   115 1.0          3 2.0          1 -3.0
28
29  REACTION
30     4     1.0     0.0  16     1.0     6.0  15     0.5     0.0
31  STEPS
32       0.008
33  TEMP
34        25.0      65.0
35  END
```

Table 15. - Printout from test problem 4 (parts A and E).

```
         DATA READ FROM DISK

ELEMENTS
SPECIES
LOOK MIN
TEST PROBLEM #4 PART A. CALCITE-DOLOMITE EQUILIBRIUM, LPCO2=-2.0, 25C.
0150011000 0 0         0.0
SOLUTION 1
PURE WATER
 0  0 0     7.00      4.00      25.0      1.00
MINERALS
FIX PCO2   2     4.00     -1.47     -4.71          0             -2.000
  35   1.00       3  -1.00
CALCITE    2     4.00     -8.47     -2.58          1              0.0
  15   1.00       4   1.00
  1.3543E+01 -4.0100E-02 -3.0000E+03  0.0         0.0
DOLOMITE   3     8.00     -17.0     -8.29          0              0.0
   4   1.00       5   1.00      15   2.00
           0     .0         .0         .0          0              0.0
SOLUTION NUMBER 1          PURE WATER


                                       TOTAL MOLALITIES OF ELEMENTS
                                       ----- ---------- -- --------

                               ELEMENT          MOLALITY          LOG MOLALITY

                               PURE WATER


                                       ----DESCRIPTION OF SOLUTION----

                                                       PH =   6.9990
                                                       PE =   4.0000
                                           ACTIVITY H2O =   1.0000
                                         IONIC STRENGTH =   0.0000
                                            TEMPERATURE =  25.0000
                                       ELECTRICAL BALANCE =   0.0
                                                     THOR =  -1.4224D-25
                                        TOTAL ALKALINITY =   1.0027D-07
                                              ITERATIONS =   5


                                           ----------------------
                                           DISTRIBUTION OF SPECIES
                                           ----------------------

        I   SPECIES    Z      MOLALITY    LOG MOLALITY     ACTIVITY    LOG ACTIVITY     GAMMA        LOG GAMMA
```

```
  1  H+        1.0    1.00268D-07    -6.9988    1.00231D-07    -6.9990    9.99628D-01    -0.0002
  2  E-       -1.0    1.00000D-04    -4.0000    1.00000D-04    -4.0000    1.00000D+00     0.0
  3  H2O       0.0    1.00000D+00    -0.0000    1.00000D+00    -0.0000    1.00000D+00     0.0
 31  OH-      -1.0    1.00268D-07    -6.9988    1.00231D-07    -6.9990    9.99628D-01    -0.0002
 33  H2 AQ     0.0    7.11214D-26   -25.1480    7.11214D-26   -25.1480    1.00000D+00     0.0000

                          ---- LOOK MIN IAP ----

                    PHASE        LOG IAP      LOG KT      LOG IAP/KT

                   O2 GAS       -42.0840     -2.9600     -39.1240
                   H2 GAS       -25.1480     -3.1500     -21.9980
STEP NUMBER  1
--------------



                         TOTAL MOLALITIES OF ELEMENTS
                         ----- ---------- -- --------

                     ELEMENT          MOLALITY          LOG MOLALITY

                     PURE WATER


                           ----PHASE BOUNDARIES----

                 PHASE     DELTA PHASE*      LOG IAP       LOG KT      LOG IAP/KT

                FIX PCO2   2.395734D-03      -3.4660      -1.4660      -2.0000
                CALCITE    1.685589D-04      -8.4749      -8.4749      -0.0000
                DOLOMITE   9.496709D-04     -17.0200     -17.0200      -0.0000

      * NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

                          ---- LOOK MIN IAP ----

                    PHASE        LOG IAP      LOG KT      LOG IAP/KT

                   CALCITE       -8.4749     -8.4749      -0.0000
                   DOLOMITE     -17.0200    -17.0200      -0.0000
                   PCO2          -3.4660     -1.4660      -2.0000
                   O2 GAS       -40.5239     -2.9600     -37.5639
                   H2 GAS       -25.9281     -3.1500     -22.7781


                         TOTAL MOLALITIES OF ELEMENTS
                         ----- ---------- -- --------
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                    ELEMENT           MOLALITY          LOG MOLALITY

                    CA              1.118230D-03          -2.9515
                    MG              9.496709D-04          -3.0224
                    C               4.463635D-03          -2.3503



                         ----DESCRIPTION OF SOLUTION----

                                         PH =   7.3891
                                         PE =   4.0000
                               ACTIVITY H2O =   0.9999
                             IONIC STRENGTH =   0.0061
                                TEMPERATURE =  25.0000
                         ELECTRICAL BALANCE =   5.9438D-12
                                       THOR =   1.7855D-02
                           TOTAL ALKALINITY =   4.1358D-03
                                 ITERATIONS =  18


                                -----------------------
                                DISTRIBUTION OF SPECIES
                                -----------------------

       I  SPECIES     Z       MOLALITY     LOG MOLALITY    ACTIVITY     LOG ACTIVITY     GAMMA       LOG GAMMA

       1  H+         1.0    4.43512D-08     -7.3531     4.08265D-08     -7.3891     9.20528D-01     -0.0360
       2  E-        -1.0    1.00000D-04     -4.0000     1.00000D-04     -4.0000     1.00000D+00      0.0
       3  H2O        0.0    9.99890D-01     -0.0000     9.99890D-01     -0.0000     1.00000D+00      0.0
       4  CA+2       2.0    1.08058D-03     -2.9663     7.82784D-04     -3.1064     7.24411D-01     -0.1400
       5  MG+2       2.0    9.15612D-04     -3.0383     6.66024D-04     -3.1765     7.27408D-01     -0.1382
      15  CO3-2     -2.0    5.90445D-06     -5.2288     4.27989D-06     -5.3686     7.24858D-01     -0.1397
      31  OH-       -1.0    2.67284D-07     -6.5730     2.46042D-07     -6.6090     9.20528D-01     -0.0360
      33  H2 AQ      0.0    1.17836D-26    -25.9287     1.18001D-26    -25.9281     1.00140D+00      0.0006
      34  HCO3-     -1.0    4.04459D-03     -2.3931     3.73197D-03     -2.4281     9.22706D-01     -0.0349
      35  H2CO3      0.0    3.41465D-04     -3.4667     3.41942D-04     -3.4660     1.00140D+00      0.0006
      75  CAOH+      1.0    5.25551D-09     -8.2794     4.83785D-09     -8.3153     9.20528D-01     -0.0360
      76  CACO3      0.0    4.75403D-06     -5.3229     4.76066D-06     -5.3223     1.00140D+00      0.0006
      77  CAHCO3+    1.0    3.28904D-05     -4.4829     3.02766D-05     -4.5189     9.20528D-01     -0.0360
      85  MGOH+      1.0    2.84749D-08     -7.5455     2.62120D-08     -7.5815     9.20528D-01     -0.0360
      86  MGCO3      0.0    2.71669D-06     -5.5660     2.72049D-06     -5.5654     1.00140D+00      0.0006
      87  MGHCO3+    1.0    3.13138D-05     -4.5043     2.88252D-05     -4.5402     9.20528D-01     -0.0360
TEST PROBLEM #4 PART E - DE-DOLOMITIZATION,DELTA T,SULFATE REDUCTION,FE PRESENT.
0042110000 4 3         0.0
MINERALS
CALCITE    2      4.00      -8.47      -2.58         1            0.0
  15   1.00         4   1.00
  1.3543E+01 -4.0100E-02 -3.0000E+03  0.0           0.0
DOLOMITE   3      8.00      -17.0      -8.29         0            0.0
   4   1.00         5   1.00       15   2.00
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PYRITE      4      .0        -18.5      11.3        0            0.0
  1  -2.00        2  -2.00        8   1.00       42   2.00
GOETHITE    3     3.00       .500      -14.5        0            0.0
 115   1.00       3   2.00        1  -3.00
            0      .0         .0         .0         0            0.0
REACTION
   4   1.000   0.0    16   1.000    6.000  15    0.500   0.0
STEPS
  .800E-02
TEMP
  25.0       65.0
STEP NUMBER  1
--------------
                        2.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


                       REACTION IS:
                                  1.00 MOLES OF CA         VALENCE =   0.0
                                  1.00 MOLES OF S          VALENCE =   6.000
                                  0.50 MOLES OF C          VALENCE =   0.0
                          35.00 = NEW TEMPERATURE (C).



                                        TOTAL MOLALITIES OF ELEMENTS
                                        ----- ---------- -- --------

                                  ELEMENT          MOLALITY          LOG MOLALITY

                                  CA            3.118230D-03          -2.5061
                                  MG            9.496709D-04          -3.0224
                                  C             5.463635D-03          -2.2625
                                  S             2.000000D-03          -2.6990


                                         ----PHASE BOUNDARIES----

                         PHASE       DELTA PHASE*       LOG IAP       LOG KT        LOG IAP/KT

                        CALCITE    -1.634148D-03       -8.5494       -8.5494       -0.0000
                        DOLOMITE    6.009634D-04      -17.2172      -17.2172       -0.0000
                        PYRITE     -2.660763D-04      -18.2112      -18.2112       -0.0000
                        GOETHITE    2.749352D-04        0.1556        0.1556       -0.0000
   * NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.


                                            ---- LOOK MIN IAP ----

                              PHASE         LOG IAP        LOG KT        LOG IAP/KT
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CALCITE        -8.5494      -8.5494      -0.0000
DOLOMITE      -17.2172     -17.2172      -0.0000
SIDERITE      -10.9112     -10.6767      -0.2345
GYPSUM         -6.0520      -4.8418      -1.2102
HEMATITE        0.3112      -4.7417       5.0529
GOETHITE        0.1556       0.1556       0.0000
FEOH3A          0.1555       4.8910      -4.7355
PYRITE        -18.2112     -18.2112      -0.0000
FES PPT        -8.8417      -3.9150      -4.9267
PCO2           -3.1603      -1.5780      -1.5823
O2 GAS        -66.3112      -3.0039     -63.3074
H2 GAS        -11.4732      -3.1918      -8.2814


                  TOTAL MOLALITIES OF ELEMENTS
                  ----- ---------- -- --------

     ELEMENT           MOLALITY          LOG MOLALITY

     CA              2.085046D-03          -2.6809
     MG              1.550634D-03          -2.8095
     FE              8.858926D-06          -5.0526
     C               5.031414D-03          -2.2983
     S               1.467848D-03          -2.8333


                  ----DESCRIPTION OF SOLUTION----

                            PH =   7.0477
                            PE =  -2.9070
                  ACTIVITY H2O =   0.9998
                IONIC STRENGTH =   0.0108
                   TEMPERATURE =  35.0000
            ELECTRICAL BALANCE =  -6.4459D-12
                          THOR =   2.8950D-02
               TOTAL ALKALINITY =   4.3535D-03
                    ITERATIONS =  25


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                      DISTRIBUTION OF SPECIES
                      -----------------------

I   SPECIES     Z       MOLALITY     LOG MOLALITY    ACTIVITY     LOG ACTIVITY      GAMMA        LOG GAMMA

1   H+         1.0    9.99174D-08      -7.0004     8.96012D-08      -7.0477     8.96753D-01     -0.0473
2   E-        -1.0    8.07212D+02       2.9070     8.07212D+02       2.9070     1.00000D+00      0.0
3   H2O        0.0    9.99835D-01      -0.0001     9.99835D-01      -0.0001     1.00000D+00      0.0
4   CA+2       2.0    1.81354D-03      -2.7415     1.19011D-03      -2.9244     6.56238D-01     -0.1829
5   MG+2       2.0    1.37130D-03      -2.8629     9.06241D-04      -3.0428     6.60864D-01     -0.1799
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     8  FE+2       2.0    8.00020D-06     -5.0969    5.17360D-06     -5.2862    6.46683D-01     -0.1893
    15  CO3-2     -2.0    3.61060D-06     -5.4424    2.37134D-06     -5.6250    6.56773D-01     -0.1826
    16  SO4-2     -2.0    1.14215D-03     -2.9423    7.45695D-04     -3.1274    6.52888D-01     -0.1852
    31  OH-       -1.0    2.59636D-07     -6.5856    2.32829D-07     -6.6330    8.96753D-01     -0.0473
    33  H2 AQ      0.0    3.35490D-12    -11.4743    3.36329D-12    -11.4732    1.00250D+00      0.0011
    34  HCO3-     -1.0    4.21242D-03     -2.3755    3.79215D-03     -2.4211    9.00231D-01     -0.0456
    35  H2CO3      0.0    6.89471D-04     -3.1615    6.91194D-04     -3.1604    1.00250D+00      0.0011
    36  CH4 AQ     0.0    5.91964D-14    -13.2277    5.93443D-14    -13.2266    1.00250D+00      0.0011
    40  HSO4-     -1.0    9.59454D-09     -8.0180    8.60394D-09     -8.0653    8.96753D-01     -0.0473
    41  S-2       -2.0    1.01067D-16    -15.9954    6.53586D-17    -16.1847    6.46683D-01     -0.1893
    42  HS-       -1.0    2.78052D-11    -10.5559    2.49344D-11    -10.6032    8.96753D-01     -0.0473
    43  H2S        0.0    5.47330D-12    -11.2618    5.48698D-12    -11.2607    1.00250D+00      0.0011
    75  CAOH+      1.0    8.28437D-09     -8.0817    7.42903D-09     -8.1291    8.96753D-01     -0.0473
    76  CACO3      0.0    5.20052D-06     -5.2840    5.21352D-06     -5.2829    1.00250D+00      0.0011
    77  CAHCO3+    1.0    7.08481D-05     -4.1497    6.35332D-05     -4.1970    8.96753D-01     -0.0473
    78  CASO4      0.0    1.95448D-04     -3.7090    1.95936D-04     -3.7079    1.00250D+00      0.0011
    85  MGOH+      1.0    4.21639D-08     -7.3751    3.78106D-08     -7.4224    8.96753D-01     -0.0473
    86  MGCO3      0.0    2.38550D-06     -5.6224    2.39146D-06     -5.6213    1.00250D+00      0.0011
    87  MGHCO3+    1.0    4.74833D-05     -4.3235    4.25808D-05     -4.3708    8.96753D-01     -0.0473
    88  MGSO4      0.0    1.29426D-04     -3.8880    1.29749D-04     -3.8869    1.00250D+00      0.0011
   105  FEOH+      1.0    4.19477D-08     -7.3773    3.76168D-08     -7.4246    8.96753D-01     -0.0473
   106  FEOH2      0.0    8.26752D-12    -11.0826    8.28818D-12    -11.0815    1.00250D+00      0.0011
   107  FEOH3-    -1.0    4.21383D-15    -14.3753    3.77876D-15    -14.4227    8.96753D-01     -0.0473
   108  FESO4      0.0    8.16766D-07     -6.0879    8.18808D-07     -6.0868    1.00250D+00      0.0011
   109  FE(HS)2    0.0    3.16872D-19    -18.4991    3.17664D-19    -18.4980    1.00250D+00      0.0011
   110  FE(HS)3-  -1.0    3.20169D-28    -27.4946    2.87113D-28    -27.5419    8.96753D-01     -0.0473
   115  FE+3       3.0    2.74542D-21    -20.5614    1.02959D-21    -20.9873    3.75022D-01     -0.4259
   116  FEOH+2     2.0    2.03686D-16    -15.6910    1.31720D-16    -15.8803    6.46683D-01     -0.1893
   117  FEOH2+     1.0    3.07060D-13    -12.5128    2.75357D-13    -12.5601    8.96753D-01     -0.0473
   118  FEOH3      0.0    3.60096D-14    -13.4436    3.60996D-14    -13.4425    1.00250D+00      0.0011
   119  FEOH4-    -1.0    4.49205D-15    -14.3476    4.02826D-15    -14.3949    8.96753D-01     -0.0473
   120  FE2OH2+4   4.0    1.79022D-30    -29.7471    3.13093D-31    -30.5043    1.74891D-01     -0.7572
   125  FESO4+     1.0    8.86249D-21    -20.0524    7.94747D-21    -20.0998    8.96753D-01     -0.0473
   126  FESO42-   -1.0    2.17035D-22    -21.6635    1.94627D-22    -21.7108    8.96753D-01     -0.0473
STEP NUMBER  2
--------------
                      4.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


                     REACTION IS:
                                1.00 MOLES OF CA          VALENCE =   0.0
                                1.00 MOLES OF S           VALENCE =   6.000
                                0.50 MOLES OF C           VALENCE =   0.0
                        45.00 = NEW TEMPERATURE (C).



                                TOTAL MOLALITIES OF ELEMENTS
                                ----- ---------- -- --------

                         ELEMENT          MOLALITY          LOG MOLALITY
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```
                 CA               5.118231D-03          -2.2909
                 MG               9.496709D-04          -3.0224
                 C                6.463636D-03          -2.1895
                 S                4.000001D-03          -2.3979


                        ----PHASE BOUNDARIES----

             PHASE     DELTA PHASE*       LOG IAP       LOG KT       LOG IAP/KT

             CALCITE   -3.397230D-03       -8.6444      -8.6444       -0.0000
             DOLOMITE   1.234576D-03      -17.4020     -17.4020       -0.0000
             PYRITE    -5.326420D-04      -17.9593     -17.9593       -0.0000
             GOETHITE   5.430157D-04       -0.1672      -0.1672       -0.0000
* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

                         ---- LOOK MIN IAP ----

                 PHASE         LOG IAP      LOG KT      LOG IAP/KT

                CALCITE         -8.6444     -8.6444       -0.0000
                DOLOMITE       -17.4020    -17.4020       -0.0000
                SIDERITE       -11.0932    -10.7955       -0.2977
                GYPSUM          -5.7162     -4.8360       -0.8803
                HEMATITE        -0.3343     -5.4292        5.0949
                GOETHITE        -0.1672     -0.1672        0.0000
                FEOH3A          -0.1673      4.8910       -5.0583
                PYRITE         -17.9593    -17.9593       -0.0000
                FES PPT         -8.8734     -3.9150       -4.9584
                PCO2            -2.9510     -1.6829       -1.2680
                O2 GAS         -63.6138     -3.0450      -60.5688
                H2 GAS         -11.3589     -3.2310       -8.1279


                       TOTAL MOLALITIES OF ELEMENTS
                       ----- ---------- -- --------

                 ELEMENT          MOLALITY          LOG MOLALITY

                 CA               2.955577D-03          -2.5294
                 MG               2.184247D-03          -2.6607
                 FE               1.037369D-05          -4.9841
                 C                5.535558D-03          -2.2568
                 S                2.934717D-03          -2.5324


                       ----DESCRIPTION OF SOLUTION----
```

```
                    PH =   6.8131
                    PE =  -2.7492
          ACTIVITY H2O =   0.9998
        IONIC STRENGTH =   0.0149
           TEMPERATURE =  45.0000
    ELECTRICAL BALANCE =  -6.1495D-12
                  THOR =   3.9771D-02
      TOTAL ALKALINITY =   4.4312D-03
            ITERATIONS =  13


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                  DISTRIBUTION OF SPECIES
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  I  SPECIES     Z      MOLALITY    LOG MOLALITY   ACTIVITY    LOG ACTIVITY     GAMMA       LOG GAMMA

  1  H+         1.0   1.74669D-07     -6.7578    1.53785D-07     -6.8131    8.80434D-01    -0.0553
  2  E-        -1.0   5.61252D+02      2.7492    5.61252D+02      2.7492    1.00000D+00     0.0
  3  H2O        0.0   9.99785D-01     -0.0001    9.99785D-01     -0.0001    1.00000D+00     0.0
  4  CA+2       2.0   2.37530D-03     -2.6243    1.45524D-03     -2.8371    6.12655D-01    -0.2128
  5  MG+2       2.0   1.81347D-03     -2.7415    1.12156D-03     -2.9502    6.18457D-01    -0.2087
  8  FE+2       2.0   8.61666D-06     -5.0647    5.17758D-06     -5.2859    6.00880D-01    -0.2212
 15  CO3-2     -2.0   2.54108D-06     -5.5950    1.55824D-06     -5.8074    6.13218D-01    -0.2124
 16  SO4-2     -2.0   2.17204D-03     -2.6631    1.32136D-03     -2.8790    6.08347D-01    -0.2158
 31  OH-       -1.0   3.05625D-07     -6.5148    2.69083D-07     -6.5701    8.80434D-01    -0.0553
 33  H2 AQ      0.0   4.36111D-12    -11.3604    4.37615D-12    -11.3589    1.00345D+00     0.0015
 34  HCO3-     -1.0   4.22756D-03     -2.3739    3.74105D-03     -2.4270    8.84919D-01    -0.0531
 35  H2CO3      0.0   1.11541D-03     -2.9526    1.11925D-03     -2.9511    1.00345D+00     0.0015
 36  CH4 AQ     0.0   2.05275D-14    -13.6877    2.05983D-14    -13.6862    1.00345D+00     0.0015
 40  HSO4-     -1.0   3.97772D-08     -7.4004    3.50212D-08     -7.4557    8.80434D-01    -0.0553
 41  S-2       -2.0   1.88010D-16    -15.7258    1.12972D-16    -15.9470    6.00880D-01    -0.2212
 42  HS-       -1.0   4.51492D-11    -10.3453    3.97509D-11    -10.4007    8.80434D-01    -0.0553
 43  H2S        0.0   4.08348D-12    -11.3890    4.09756D-12    -11.3875    1.00345D+00     0.0015
 75  CAOH+      1.0   1.26752D-08     -7.8970    1.11597D-08     -7.9523    8.80434D-01    -0.0553
 76  CACO3      0.0   5.79034D-06     -5.2373    5.81031D-06     -5.2358    1.00345D+00     0.0015
 77  CAHCO3+    1.0   1.18238D-04     -3.9272    1.04101D-04     -3.9825    8.80434D-01    -0.0553
 78  CASO4      0.0   4.56238D-04     -3.3408    4.57812D-04     -3.3393    1.00345D+00     0.0015
 85  MGOH+      1.0   6.83240D-08     -7.1654    6.01548D-08     -7.2207    8.80434D-01    -0.0553
 86  MGCO3      0.0   2.25988D-06     -5.6459    2.26767D-06     -5.6444    1.00345D+00     0.0015
 87  MGHCO3+    1.0   6.37584D-05     -4.1955    5.61351D-05     -4.2508    8.80434D-01    -0.0553
 88  MGSO4      0.0   3.04686D-04     -3.5161    3.05737D-04     -3.5147    1.00345D+00     0.0015
105  FEOH+      1.0   4.90495D-08     -7.3094    4.31849D-08     -7.3647    8.80434D-01    -0.0553
106  FEOH2      0.0   1.21560D-11    -10.9152    1.21979D-11    -10.9137    1.00345D+00     0.0015
107  FEOH3-    -1.0   4.02284D-15    -14.3955    3.54185D-15    -14.4508    8.80434D-01    -0.0553
108  FESO4      0.0   1.70797D-06     -5.7675    1.71386D-06     -5.7660    1.00345D+00     0.0015
109  FE(HS)2    0.0   1.03342D-19    -18.9857    1.03698D-19    -18.9842    1.00345D+00     0.0015
110  FE(HS)3-  -1.0   6.07983D-29    -28.2161    5.35289D-29    -28.2714    8.80434D-01    -0.0553
115  FE+3       3.0   7.78867D-21    -20.1085    2.47591D-21    -20.6063    3.17887D-01    -0.4977
116  FEOH+2     2.0   5.23766D-16    -15.2809    3.14721D-16    -15.5021    6.00880D-01    -0.2212
117  FEOH2+     1.0   2.55287D-13    -12.5930    2.24764D-13    -12.6483    8.80434D-01    -0.0553
118  FEOH3      0.0   1.71087D-14    -13.7668    1.71677D-14    -13.7653    1.00345D+00     0.0015
119  FEOH4-    -1.0   1.26768D-15    -14.8970    1.11611D-15    -14.9523    8.80434D-01    -0.0553
120  FE2OH2+4   4.0   9.42642D-30    -29.0257    1.22885D-30    -29.9105    1.30362D-01    -0.8848
```

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      125  FESO4+    1.0     4.70130D-20    -19.3278      4.13919D-20    -19.3831      8.80434D-01     -0.0553
      126  FESO42-  -1.0     2.11364D-21    -20.6750      1.86092D-21    -20.7303      8.80434D-01     -0.0553
 STEP NUMBER  3
 --------------
                    6.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


                   REACTION IS:
                                  1.00 MOLES OF CA        VALENCE =   0.0
                                  1.00 MOLES OF S         VALENCE =   6.000
                                  0.50 MOLES OF C         VALENCE =   0.0
                      55.00 = NEW TEMPERATURE (C).



                              TOTAL MOLALITIES OF ELEMENTS
                              ----- ---------- -- --------

                       ELEMENT        MOLALITY         LOG MOLALITY

                       CA          7.118231D-03         -2.1476
                       MG          9.496709D-04         -3.0224
                       C           7.463636D-03         -2.1270
                       S           6.000001D-03         -2.2218


                               ----PHASE BOUNDARIES----

                   PHASE     DELTA PHASE*     LOG IAP      LOG KT      LOG IAP/KT

                  CALCITE   -5.525535D-03     -8.7581     -8.7581      -0.0000
                  DOLOMITE   2.024228D-03    -17.5755    -17.5755      -0.0000
                  PYRITE    -7.993251D-04    -17.7228    -17.7228      -0.0000
                  GOETHITE   8.094533D-04     -0.4703     -0.4703      -0.0000

   * NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.


                                ---- LOOK MIN IAP ----

                      PHASE        LOG IAP      LOG KT      LOG IAP/KT

                     CALCITE       -8.7581     -8.7581      -0.0000
                     DOLOMITE     -17.5755    -17.5755      -0.0000
                     SIDERITE     -11.3124    -10.9070      -0.4054
                     GYPSUM        -5.5474     -4.8305      -0.7169
                     HEMATITE      -0.9405     -6.0749       5.1344
                     GOETHITE      -0.4703     -0.4703      -0.0000
                     FEOH3A        -0.4704      4.8910      -5.3614
                     PYRITE       -17.7228    -17.7228      -0.0000
                     FES PPT       -8.8639     -3.9150      -4.9489
```

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PCO2           -2.7944        -1.7815        -1.0129
O2 GAS        -61.1856        -3.0836       -58.1020
H2 GAS        -11.1992        -3.2679        -7.9313


                  TOTAL MOLALITIES OF ELEMENTS
                  ----- ---------- -- --------

      ELEMENT           MOLALITY         LOG MOLALITY

      CA             3.616923D-03          -2.4417
      MG             2.973899D-03          -2.5267
      FE             1.012816D-05          -4.9945
      C              5.986556D-03          -2.2228
      S              4.401351D-03          -2.3564



                  ----DESCRIPTION OF SOLUTION----

                              PH =   6.6415
                              PE =  -2.6759
                    ACTIVITY H2O =   0.9997
                  IONIC STRENGTH =   0.0186
                     TEMPERATURE =  55.0000
              ELECTRICAL BALANCE =  -2.1748D-12
                            THOR =   5.0375D-02
                 TOTAL ALKALINITY =   4.3996D-03
                       ITERATIONS =  13


                      ----------------------
                      DISTRIBUTION OF SPECIES
                      ----------------------

 I  SPECIES    Z     MOLALITY    LOG MOLALITY    ACTIVITY    LOG ACTIVITY     GAMMA       LOG GAMMA

 1  H+        1.0  2.63180D-07    -6.5797     2.28285D-07     -6.6415     8.67411D-01    -0.0618
 2  E-       -1.0  4.74111D+02     2.6759     4.74111D+02      2.6759     1.00000D+00     0.0
 3  H2O       0.0  9.99737D-01    -0.0001     9.99737D-01     -0.0001     1.00000D+00     0.0
 4  CA+2      2.0  2.71864D-03    -2.5656     1.57577D-03     -2.8025     5.79616D-01    -0.2369
 5  MG+2      2.0  2.34438D-03    -2.6300     1.37462D-03     -2.8618     5.86349D-01    -0.2318
 8  FE+2      2.0  7.76724D-06    -5.1097     4.39710D-06     -5.3568     5.66109D-01    -0.2471
15  CO3-2    -2.0  1.90913D-06    -5.7192     1.10767D-06     -5.9556     5.80197D-01    -0.2364
16  SO4-2    -2.0  3.13324D-03    -2.5040     1.80020D-03     -2.7447     5.74549D-01    -0.2407
31  OH-      -1.0  3.97571D-07    -6.4006     3.44858D-07     -6.4624     8.67411D-01    -0.0618
33  H2 AQ     0.0  6.29487D-12   -11.2010     6.32189D-12    -11.1992     1.00429D+00     0.0019
34  HCO3-    -1.0  4.12435D-03    -2.3846     3.59956D-03     -2.4438     8.72758D-01    -0.0591
35  H2CO3     0.0  1.59833D-03    -2.7963     1.60519D-03     -2.7945     1.00429D+00     0.0019
36  CH4 AQ    0.0  1.03648D-14   -13.9844     1.04093D-14    -13.9826     1.00429D+00     0.0019
40  HSO4-    -1.0  1.10157D-07    -6.9580     9.55513D-08     -7.0198     8.67411D-01    -0.0618
```

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    41  S-2      -2.0   4.30343D-16   -15.3662   2.43621D-16   -15.6133   5.66109D-01   -0.2471
    42  HS-      -1.0   8.18752D-11   -10.0868   7.10195D-11   -10.1486   8.67411D-01   -0.0618
    43  H2S       0.0   3.19652D-12   -11.4953   3.21024D-12   -11.4935   1.00429D+00    0.0019
    75  CAOH+     1.0   1.89081D-08    -7.7234   1.64011D-08    -7.7851   8.67411D-01   -0.0618
    76  CACO3     0.0   6.55162D-06    -5.1837   6.57974D-06    -5.1818   1.00429D+00    0.0019
    77  CAHCO3+   1.0   1.69842D-04    -3.7700   1.47323D-04    -3.8317   8.67411D-01   -0.0618
    78  CASO4     0.0   7.21867D-04    -3.1415   7.24965D-04    -3.1397   1.00429D+00    0.0019
    85  MGOH+     1.0   1.20386D-07    -6.9194   1.04424D-07    -6.9812   8.67411D-01   -0.0618
    86  MGCO3     0.0   2.29382D-06    -5.6394   2.30367D-06    -5.6376   1.00429D+00    0.0019
    87  MGHCO3+   1.0   8.32834D-05    -4.0794   7.22410D-05    -4.1412   8.67411D-01   -0.0618
    88  MGSO4     0.0   5.43823D-04    -3.2645   5.46157D-04    -3.2627   1.00429D+00    0.0019
   105  FEOH+     1.0   5.38103D-08    -7.2691   4.66756D-08    -7.3309   8.67411D-01   -0.0618
   106  FEOH2     0.0   1.85447D-11   -10.7318   1.86243D-11   -10.7299   1.00429D+00    0.0019
   107  FEOH3-   -1.0   4.56596D-15   -14.3405   3.96056D-15   -14.4022   8.67411D-01   -0.0618
   108  FESO4     0.0   2.30710D-06    -5.6369   2.31700D-06    -5.6351   1.00429D+00    0.0019
   109  FE(HS)2   0.0   4.07124D-20   -19.3903   4.08871D-20   -19.3884   1.00429D+00    0.0019
   110  FE(HS)3- -1.0   1.65794D-29   -28.7804   1.43811D-29   -28.8422   8.67411D-01   -0.0618
   115  FE+3      3.0   1.44994D-20   -19.8387   4.03064D-21   -20.3946   2.77987D-01   -0.5560
   116  FEOH+2    2.0   1.00640D-15   -14.9972   5.69734D-16   -15.2443   5.66109D-01   -0.2471
   117  FEOH2+    1.0   1.91412D-13   -12.7180   1.66033D-13   -12.7798   8.67411D-01   -0.0618
   118  FEOH3     0.0   8.50617D-15   -14.0703   8.54268D-15   -14.0684   1.00429D+00    0.0019
   119  FEOH4-   -1.0   4.31298D-16   -15.3652   3.74113D-16   -15.4270   8.67411D-01   -0.0618
   120  FE2OH2+4  4.0   2.75796D-29   -28.5594   2.83261D-30   -29.5478   1.02707D-01   -0.9884
   125  FESO4+    1.0   1.27783D-19   -18.8935   1.10841D-19   -18.9553   8.67411D-01   -0.0618
   126  FESO42-  -1.0   8.09156D-21   -20.0920   7.01871D-21   -20.1537   8.67411D-01   -0.0618
STEP NUMBER  4
-------------
                   8.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


                  REACTION IS:
                             1.00 MOLES OF CA         VALENCE =   0.0
                             1.00 MOLES OF S          VALENCE =   6.000
                             0.50 MOLES OF C          VALENCE =   0.0
                     65.00 = NEW TEMPERATURE (C).



                             TOTAL MOLALITIES OF ELEMENTS
                             ----- ---------- -- --------

                         ELEMENT          MOLALITY         LOG MOLALITY

                         CA             9.118231D-03         -2.0401
                         MG             9.496709D-04         -3.0224
                         C              8.463636D-03         -2.0724
                         S              8.000001D-03         -2.0969


                              ----PHASE BOUNDARIES----
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   PHASE      DELTA PHASE*       LOG IAP       LOG KT       LOG IAP/KT

  CALCITE   -8.220766D-03       -8.8888       -8.8888       -0.0000
  DOLOMITE   3.081645D-03      -17.7388      -17.7388       -0.0000
  PYRITE    -1.066094D-03      -17.5002      -17.5002       -0.0000
  GOETHITE   1.074744D-03       -0.7555       -0.7555       -0.0000

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

                        ---- LOOK MIN IAP ----

            PHASE         LOG IAP       LOG KT       LOG IAP/KT

           CALCITE        -8.8888       -8.8888       -0.0000
           DOLOMITE      -17.7388      -17.7388       -0.0000
           SIDERITE      -11.5627      -11.0120       -0.5508
           GYPSUM         -5.4636       -4.8254       -0.6382
           HEMATITE       -1.5108       -6.6824        5.1716
           GOETHITE       -0.7555       -0.7555        0.0000
           FEOH3A         -0.7556        4.8910       -5.6466
           PYRITE        -17.5002      -17.5002       -0.0000
           FES PPT        -8.8330       -3.9150       -4.9180
           PCO2           -2.6723       -1.8742       -0.7981
           O2  GAS       -58.9596       -3.1199      -55.8397
           H2  GAS       -11.0195       -3.3025       -7.7170


                     TOTAL MOLALITIES OF ELEMENTS
                     ----- ---------- -- --------

              ELEMENT         MOLALITY          LOG MOLALITY

              CA            3.979109D-03          -2.4002
              MG            4.031316D-03          -2.3946
              FE            8.649850D-06          -5.0630
              C             6.406159D-03          -2.1934
              S             5.867813D-03          -2.2315



                     ----DESCRIPTION OF SOLUTION----

                              PH =   6.5167
                              PE =  -2.6582
                    ACTIVITY H2O =   0.9997
                 IONIC STRENGTH =   0.0220
                    TEMPERATURE =  65.0000
             ELECTRICAL BALANCE =   1.0877D-11
                           THOR =   6.0849D-02
                TOTAL ALKALINITY =   4.3031D-03
                      ITERATIONS =  13
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                                   -----------------------
                                   DISTRIBUTION OF SPECIES
                                   -----------------------

  I  SPECIES     Z      MOLALITY    LOG MOLALITY   ACTIVITY   LOG ACTIVITY    GAMMA       LOG GAMMA

  1  H+         1.0   3.55472D-07    -6.4492    3.04306D-07    -6.5167   8.56062D-01    -0.0675
  2  E-        -1.0   4.55186D+02     2.6582    4.55186D+02     2.6582   1.00000D+00     0.0
  3  H2O        0.0   9.99692D-01    -0.0001    9.99692D-01    -0.0001   1.00000D+00     0.0
  4  CA+2       2.0   2.81780D-03    -2.5501    1.55548D-03    -2.8081   5.52019D-01    -0.2580
  5  MG+2       2.0   3.03931D-03    -2.5172    1.70060D-03    -2.7694   5.59537D-01    -0.2522
  8  FE+2       2.0   6.13593D-06    -5.2121    3.29535D-06    -5.4821   5.37057D-01    -0.2700
 15  CO3-2     -2.0   1.50297D-06    -5.8230    8.30580D-07    -6.0806   5.52624D-01    -0.2576
 16  SO4-2     -2.0   4.04946D-03    -2.3926    2.21232D-03    -2.6552   5.46325D-01    -0.2625
 31  OH-       -1.0   5.53478D-07    -6.2569    4.73812D-07    -6.3244   8.56062D-01    -0.0675
 33  H2 AQ      0.0   9.51244D-12   -11.0217    9.56068D-12   -11.0195   1.00507D+00     0.0022
 34  HCO3-     -1.0   3.95185D-03    -2.4032    3.40728D-03    -2.4676   8.62199D-01    -0.0644
 35  H2CO3      0.0   2.11540D-03    -2.6746    2.12613D-03    -2.6724   1.00507D+00     0.0022
 36  CH4 AQ     0.0   6.23652D-15   -14.2051    6.26815D-15   -14.2029   1.00507D+00     0.0022
 40  HSO4-     -1.0   2.48477D-07    -6.6047    2.12712D-07    -6.6722   8.56062D-01    -0.0675
 41  S-2       -2.0   1.12515D-15   -14.9488    6.04268D-16   -15.2188   5.37057D-01    -0.2700
 42  HS-       -1.0   1.58461D-10    -9.8001    1.35652D-10    -9.8676   8.56062D-01    -0.0675
 43  H2S        0.0   2.58203D-12   -11.5880    2.59512D-12   -11.5858   1.00507D+00     0.0022
 75  CAOH+      1.0   2.74247D-08    -7.5619    2.34773D-08    -7.6294   8.56062D-01    -0.0675
 76  CACO3      0.0   7.52169D-06    -5.1237    7.55984D-06    -5.1215   1.00507D+00     0.0022
 77  CAHCO3+    1.0   2.18421D-04    -3.6607    1.86982D-04    -3.7282   8.56062D-01    -0.0675
 78  CASO4      0.0   9.35338D-04    -3.0290    9.40081D-04    -3.0268   1.00507D+00     0.0022
 85  MGOH+      1.0   2.27785D-07    -6.6425    1.94998D-07    -6.7100   8.56062D-01    -0.0675
 86  MGCO3      0.0   2.47920D-06    -5.6057    2.49178D-06    -5.6035   1.00507D+00     0.0022
 87  MGHCO3+    1.0   1.08989D-04    -3.9626    9.33012D-05    -4.0301   8.56062D-01    -0.0675
 88  MGSO4      0.0   8.80314D-04    -3.0554    8.84778D-04    -3.0532   1.00507D+00     0.0022
105  FEOH+      1.0   5.57737D-08    -7.2536    4.77458D-08    -7.3211   8.56062D-01    -0.0675
106  FEOH2      0.0   2.85415D-11   -10.5445    2.86862D-11   -10.5423   1.00507D+00     0.0022
107  FEOH3-    -1.0   5.78310D-15   -14.2378    4.95069D-15   -14.3053   8.56062D-01    -0.0675
108  FESO4      0.0   2.45811D-06    -5.6094    2.47058D-06    -5.6072   1.00507D+00     0.0022
109  FE(HS)2    0.0   1.81324D-20   -19.7415    1.82243D-20   -19.7393   1.00507D+00     0.0022
110  FE(HS)3-  -1.0   5.77455D-30   -29.2385    4.94337D-30   -29.3060   8.56062D-01    -0.0675
115  FE+3       3.0   2.00538D-20   -19.6978    4.95156D-21   -20.3053   2.46914D-01    -0.6075
116  FEOH+2     2.0   1.56670D-15   -14.8050    8.41408D-16   -15.0750   5.37057D-01    -0.2700
117  FEOH2+     1.0   1.34076D-13   -12.8727    1.14777D-13   -12.9401   8.56062D-01    -0.0675
118  FEOH3      0.0   4.40763D-15   -14.3558    4.42998D-15   -14.3536   1.00507D+00     0.0022
119  FEOH4-    -1.0   1.70001D-16   -15.7695    1.45532D-16   -15.8370   8.56062D-01    -0.0675
120  FE2OH2+4   4.0   5.33345D-29   -28.2730    4.43700D-30   -29.3529   8.31919D-02    -1.0799
125  FESO4+     1.0   2.33396D-19   -18.6319    1.99801D-19   -18.6994   8.56062D-01    -0.0675
126  FESO42-   -1.0   1.87398D-20   -19.7272    1.60424D-20   -19.7947   8.56062D-01    -0.0675
```

Test Problem 5. - Defining Reaction Paths

In this final example we demonstrate the use of PHREEQE in defining a reaction path and mass transfer in a chemical system in which an irreversible reaction is occurring. The program was not written with this specific objective in mind, and as a result use of PHREEQE as a general "reaction path-finding" program is cumbersome and requires a good deal of manipulation by the user. This is not necessarily bad, as it forces a careful consideration of the chemistry of the system under consideration during the path simulation. Computer programs are available that have the general "path-finding" logic incorporated in the program (Helgeson and others, 1970, Wolery, 1979). In the following section, we use a specific problem in a relatively simple chemical system to illustrate the logical approach necessary to use PHREEQE to define reaction paths.

We have considered a limited (and simplified) problem which is the weathering of potassium feldspar in an (initially) pure water closed system at 25°C. Application of PHREEQE to more complex (and more realistic) path finding problems should be evident from this test case. Calculation of the feldspar weathering reaction path was originally addressed by Helgeson and others (1969), and is reconsidered using the recent revision in pertinent thermodynamic data (Robie and others, 1978).

The problem is limited to the isothermal (25°C) chemical system K_2O-Al_2O_3-SiO_2-H_2O and we will determine the reaction path and mass transfer considering only the phases gibbsite, kaolinite, muscovite and microcline. All thermodynamic data for these phases are taken from Robie and others (1978), and are summarized as follows (table 16):

Table 16. - Selected Thermodynamic Data in the System $K_2O-Al_2O_3-SiO_2-H_2O$

Mineral	Reaction	Log K	ΔH^o_r (kcal/mole)
Gibbsite	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	8.049	-22.792
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$	5.708	-35.306
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = 3Al^{3+} + K^+ + 3H_4SiO_4$	12.970	-59.377
Microcline	$KAlSi_3O_8 + 4H^+ + 4H_2O = Al^{3+} + K^+ + 3H_4SiO_4$	0.875	-12.467

The phase relations in this system as a function of a_{K^+}, a_{H^+}, and $a_{H_4SiO_4}$ have been constructed from the data of Robie and others (1978), (figure 2). Although we already have an understanding of this reaction path (Helgeson and others, 1969), it is instructive to address the problem in a general sense to show the application of PHREEQE to problems in reaction path definition.

In this problem we consider the possibility that as the irreversible reaction proceeds, the aqueous phase may become undersaturated with an original product phase. Our problem is analogous to reacting microcline crystals in a beaker of pure water and following the changes in masses of reactants and products, and the composition of the aqueous solution. Reaction progress is followed in terms of moles of microcline dissolved. All other heterogeneous reactions are at equilibrium (a partial equilibrium system). The reaction ends when the aqueous phase reaches equilibrium with microcline (overall equilibrium).

The problem is in two parts, A and B. Part A determines the intersections of the reaction path with phase boundaries in the system, and once the intersections are defined, part B defines the reaction paths across stability fields between phase boundaries.

Part A. - Location of phase boundary intersections.

The logical definition of the thermodynamically stable intersections of phase boundaries on the reaction path is determined in 15 simulations. Input cards for the 15 PHREEQE runs are listed in table 17, and selected output for each run is given in table 18.

Using a value for IOPT(3) of 6, the irreversible reaction (defined by REACTION input) is added to solution (or subtracted from solution) as required to reach equilibrium with the first mineral included under MINERALS input. Although all minerals under MINERALS input will be in equilibrium with the aqueous phase, the amount of reaction added (or removed) determines the point in mass transfer where the first mineral listed under MINERALS input has zero mass in the system. Other minerals included under MINERALS input will likely have dissolved or precipitated during the irreversible reaction to reach equilibrium with the first mineral.

Cards 1-25 of table 17 can be used as an example for all 15 of the phase boundary problems. Cards 1-16 define pure water as the starting solution, add muscovite and microcline to the LOOK MIN data base, and change LOOK MIN data for gibbsite and kaolinite to data given in table 16. The amount of reaction added to reach the gibbsite phase boundary is found using cards 17-25. Particular details are as follows:

1. IOPT(2), card 18, could be zero or 1 because the starting solution, pure water, was solved earlier and saved in SOLUTION 1.

2. IOPT(3) is 6 which is the reaction path option discussed above.

3. All other options are zero for this particular problem which defines an isothermal system (IOPT(4) = 0), independent of redox (IOPT(5) = 0), and Debye-Hückel activity coefficients (IOPT(6) = 0).

4. NSTEP is 1 for use of IOPT(3) = 6.

5. There are 3 constituents in the irreversible reaction (NCOMPS = 3; K, Al, and Si), defining the stoichiometry of microcline.

6. The irreversible reaction will be added to the starting solution until equilibrium with gibbsite (the first phase in MINERALS input) is found.

Beginning with pure water, runs 1-4 (table 18) show that as microcline dissolves, gibbsite is the first phase boundary encountered, because paths to kaolinite, muscovite or microcline result in supersatured (metastable) solutions. (See saturation index information for runs 2-4, table 18.)

Table 17. - Card images of input data set for test problem 5, part A.

```
CARD NO.                                  COLUMN

             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

  1  TEST PROBLEM #5 PART A  FIND PHASE BOUNDARY INTERSECTIONS IN K-SPAR WEATHERING.
  2  010000100  0 0
  3  SOLUTION 1
  4  PURE WATER
  5   0  0 0          7.0       4.0      25.0       1.0
  6  LOOK MIN
  7  GIBBSITE   3          0.0     8.049   -22.792     0
  8    10        1.0   3        3.0   1       -3.0
  9  KAOLINIT   4          0.0     5.708   -35.306     0
 10    10        2.0   3        1.0  13        2.0   1       -6.0
 11  MUSCOVIT   4          0.0     12.97   -59.377     0
 12    10        3.0  13        3.0   7        1.0   1      -10.0
 13  MICROCLN   5          0.0     0.875   -12.467     0
 14    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
 15
 16  END
 17  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE SATURATION.
 18  0160000000 1 3
 19  MINERALS
 20  GIBBSITE   3          0.0     8.049   -22.792     0
 21    10        1.0   3        3.0   1       -3.0
 22
 23  REACTION
 24     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
 25  END
 26  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH KAOLINITE SATURATION.
 27  0160000000 1 3
 28  MINERALS
 29  KAOLINIT   4          0.0     5.708   -35.306     0
 30    10        2.0   3        1.0  13        2.0   1       -6.0
 31
 32  REACTION
 33     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
 34  END
 35  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH MUSCOVITE SATURATION.
 36  0160000000 1 3
 37  MINERALS
 38  MUSCOVIT   4          0.0     12.97   -59.377     0
 39    10        3.0  13        3.0   7        1.0   1      -10.0
 40
 41  REACTION
 42     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
 43  END
 44  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH K-SPAR SATURATION.
 45  0160000000 1 3
 46  MINERALS
 47  MICROCLN   5          0.0     0.875   -12.467     0
 48    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
 49
 50  REACTION

     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
```

```
CARD NO.                              COLUMN

               10        20        30        40        50        60        70        80
      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

 51      7     1.0    0.0   10     1.0     0.0  13     3.0     0.0
 52   END
 53   FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE-KAOLINITE PHASE BOUNDARY.
 54   0160000000 1 3
 55   MINERALS
 56   KAOLINIT   4          0.0     5.708   -35.306     0
 57     10         2.0   3        1.0  13         2.0   1       -6.0
 58   GIBBSITE   3          0.0     8.049   -22.792     0
 59     10         1.0   3        3.0   1       -3.0
 60
 61   REACTION
 62      7     1.0    0.0   10     1.0     0.0  13     3.0     0.0
 63   END
 64   FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE-MUSCOVITE PAHSE BOUNDARY.
 65   0160000000 1 3
 66   MINERALS
 67   MUSCOVIT   4          0.0     12.97   -59.377     0
 68     10         3.0  13        3.0   7         1.0   1      -10.0
 69   GIBBSITE   3          0.0     8.049   -22.792     0
 70     10         1.0   3        3.0   1       -3.0
 71
 72   REACTION
 73      7     1.0    0.0   10     1.0     0.0  13     3.0     0.0
 74   END
 75   FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE - K-SPAR PHASE BOUNDARY.
 76   0160000000 1 3
 77   MINERALS
 78   MICROCLN   5          0.0     0.875   -12.467     0
 79     10         1.0  13        3.0   7         1.0   3       -4.0   1       -4.0
 80   GIBBSITE   3          0.0     8.049   -22.792     0
 81     10         1.0   3        3.0   1       -3.0
 82
 83   REACTION
 84      7     1.0    0.0   10     1.0     0.0  13     3.0     0.0
 85   END
 86   FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE-KAOLINITE-MUSCOVITE.
 87   0160000000 1 3
 88   MINERALS
 89   MUSCOVIT   4          0.0     12.97   -59.377     0
 90     10         3.0  13        3.0   7         1.0   1      -10.0
 91   KAOLINIT   4          0.0     5.708   -35.306     0
 92     10         2.0   3        1.0  13         2.0   1       -6.0
 93   GIBBSITE   3          0.0     8.049   -22.792     0
 94     10         1.0   3        3.0   1       -3.0
 95
 96   REACTION
 97   /  7     1.0    0.0   10     1.0     0.0  13     3.0     0.0
 98   END
 99   FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE-KAOLINITE-MICROCLINE.
100   0160000000 1 3

      +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
               10        20        30        40        50        60        70        80
```

```
CARD NO.                               COLUMN

             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

101  MINERALS
102  MICROCLN   5          0.0     0.875   -12.467     0
103    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
104  KAOLINIT   4          0.0     5.708   -35.306     0
105    10        2.0   3        1.0  13        2.0   1       -6.0
106  GIBBSITE   3          0.0     8.049   -22.792     0
107    10        1.0   3        3.0   1       -3.0
108
109  REACTION
110     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
111  END
112  FIND AMOUNT OF K-SPAR DISSOLVED AS PATH ENTERS KAOLINITE STABILITY FIELD.
113  0160000000 1 3
114  MINERALS
115  GIBBSITE   3          0.0     8.049   -22.792     0
116    10        1.0   3        3.0   1       -3.0
117  KAOLINIT   4          0.0     5.708   -35.306     0
118    10        2.0   3        1.0  13        2.0   1       -6.0
119
120  REACTION
121     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
122  END
123  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH K-MICA - KAOLINITE PHASE BOUNDARY.
124  0160000000 1 3
125  MINERALS
126  MUSCOVIT   4          0.0     12.97   -59.377     0
127    10        3.0  13        3.0   7        1.0   1      -10.0
128  KAOLINIT   4          0.0     5.708   -35.306     0
129    10        2.0   3        1.0  13        2.0   1       -6.0
130
131  REACTION
132     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
133  END
134  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH K-SPAR - KAOLINITE PHASE BOUNDARY.
135  0160000000 1 3
136  MINERALS
137  MICROCLN   5          0.0     0.875   -12.467     0
138    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
139  KAOLINIT   4          0.0     5.708   -35.306     0
140    10        2.0   3        1.0  13        2.0   1       -6.0
141
142  REACTION
143     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
144  END
145  DISSOLVE K-SPAR TO REACH OVERALL K-SPAR - KAOLINITE - MUSCOVITE EQUILIBRIUM.
146  016000000  1 3
147  MINERALS
148  MICROCLN   5          0.0     0.875   -12.467     0
149    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
150  KAOLINIT   4          0.0     5.708   -35.306     0

     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
```

```
CARD NO.                                  COLUMN

             1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
     +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

151    10        2.0   3        1.0  13        2.0   1       -6.0
152  MUSCOVIT   4          0.0     12.97   -59.377     0
153    10        3.0  13        3.0   7        1.0   1      -10.0
154
155  REACTION
156     7     1.0     0.0  10      1.0     0.0  13      3.0     0.0
157  END
158  FIND AMOUNT OF K-SPAR DISSOLVED AS PATH ENTERS MUSCOVITE STABILITY FIELD.
159  0160000000 1 3
160  MINERALS
161  KAOLINIT   4          0.0     5.708   -35.306     0
162    10        2.0   3        1.0  13        2.0   1       -6.0
163  MUSCOVIT   4          0.0     12.97   -59.377     0
164    10        3.0  13        3.0   7        1.0   1      -10.0
165
166  REACTION
167     7     1.0     0.0  10      1.0     0.0  13      3.0     0.0
168  END
169  DISSOLVE K-SPAR TO REACH MUSCOVITE - K-SPAR EQUILIBRIUM.
170  016000000  1 3
171  MINERALS
172  MICROCLN   5          0.0     0.875   -12.467     0
173    10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
174  MUSCOVIT   4          0.0     12.97   -59.377     0
175    10        3.0  13        3.0   7        1.0   1      -10.0
176
177  REACTION
178     7     1.0     0.0  10      1.0     0.0  13      3.0     0.0
179  END
```

Table 18. - Location of phase boundary and reaction path intersections in test problem 5 (Part A).

Run	Reaction from pure water to [1/]	microcline µmoles [2/] dissolved per kg H_2O	pH	Log $\frac{a_{K^+}}{a_{H^+}}$	Log $a_{H_4SiO_4}$
1	Gibbsite	0.02395061	7.0267	-0.5942	-7.1441
2	Kaolinite	0.2528243	7.2118	0.6143	-6.1209
3	Muscovite	0.9530882	7.4534	1.4320	-5.5452
4	Microcline	19.99020	8.0171	3.3156	-4.2274
5	Kaolinite - Gibbsite	2.173389	8.2613	2.5977	-5.1950
6	Muscovite - Gibbsite	5.163625	8.6010	3.3128	-4.8299
7	Microcline - Gibbsite	39.91104	9.2371	4.8350	-4.0030
8	Muscovite - Kaolinite - Gibbsite	17.55088	9.1658	4.4080	-5.1950
9	Microcline - Kaolinite - Gibbsite	1879.435	11.1583	8.4111	-5.1951
10	Gibbsite - Kaolinite	3.137330	8.4200	2.9157	-5.1950
11	Muscovite - Kaolinite	19.16325	9.1278	4.4080	-4.4774
12	Microcline - Kaolinite	113.5645	9.5936	5.6435	-3.8112
13	Microcline - Muscovite - Kaolinite	341.0297	8.7375	4.4079	-3.1935
14	Kaolinite - Muscovite	30.98670	9.0941	4.4080	-4.2664
15	Microcline - Muscovite	181.5095	9.4499	5.5272	-3.5666

[1/] Equilibrium phases. Simulations were performed so that each underlined mineral is in equilibrium with the aqueous phase but has zero mass in the system. The aqueous phase is in equilibrium with each mineral tested.

[2/] Microcline dissolved, in µmoles per kg H_2O, to reach the defined phase boundaries.

[3/] Mass of gibbsite, kaolinite, and muscovite precipitated (negative) or dissolved (positive) in reaching the defined phase boundaries (µmol/kg H_2O).

Table 18. - (continued)

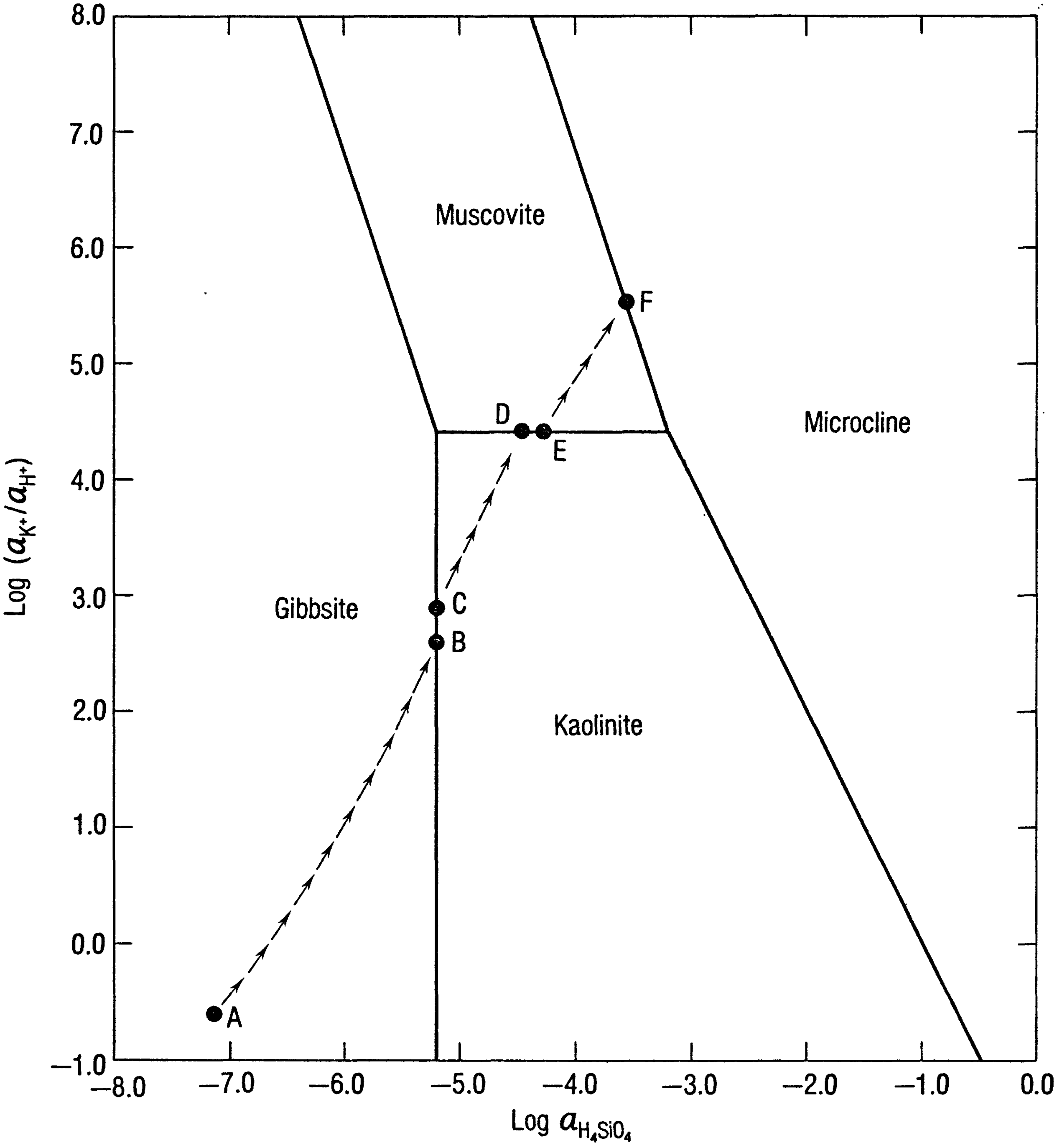
Mass µmol/kg H_2O 3/			Saturation Index 4/				Card 5/ numbers from table 17	Point 6/ identifier figure 2
Gibbsite	Kaolinite	Muscovite	Gibbsite	Kaolinite	Muscovite	Microcline		
0.0	0.0	0.0	0.0	-3.8982	-10.8495	-14.8525	17-25	A
0.0	0.0	0.0	0.9259	0.0	-3.7937	-9.6485	26-34	*
0.0	0.0	0.0	1.3422	1.9840	0.0	-6.6874	35-43	*
0.0	0.0	0.0	2.1925	6.3203	8.3881	0.0	44-52	*
-1.957486	0.0	0.0	0.0	0.0	-1.8103	-5.8133	53-63	B
-4.704494	0.0	0.0	0.0	0.7301	0.0	-4.0030	64-74	*
-37.95318	0.0	0.0	0.0	2.3840	4.0030	0.0	75-85	*
29.26792	-22.57980	0.0	0.0	0.0	0.0	-4.0030	86-98	**
3769.198	-2739.717	0.0	0.0	0.0	4.0031	0.0	99-111	**
0.0	-1.415530	0.0	0.0	0.0	-1.4924	-5.4954	112-122	C
0.0	-9.435881	0.0	-0.7176	0.0	0.0	-2.5679	123-131	D
0.0	-56.69014	0.0	-1.3838	0.0	1.2355	0.0	134-144	*
0.0	270.2347	-293.8309	-2.0015	0.0	0.0	0.0	145-157	**
0.0	0.0	-10.27355	-0.9286	0.0	0.0	-2.1457	158-168	E
0.0	0.0	-60.49252	-2.0015	-0.7461	0.0	0.0	169-179	F

4/ Saturation Index = log (IAP/K).

5/ Card numbers in table 17 used to calculate tabulated results.

6/ Points A-F define the intersections of the reaction path with phase boundaries (see figure 2). Other simulations are shown to generate metastable solutions (*) or dissolve masses of former product minerals which are larger than their mass known to be present in the system (**).

Figure 2. - Equilibrium diagram for gibbsite, kaolinite, muscovite, and microcline at 25°C. Constructed from thermodynamic data of Robie and others (1978). Stable phase boundary intersections (test problem 5, part A) and reaction paths across stability fields (test problem 5, part B) are shown.


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
−8.0
−7.0
−6.0
−5.0
−4.0
−3.0
−2.0
−1.0
0.0
Log (a_{K^+}/a_{H^+})
Log $a_{H_4SiO_4}$
Muscovite
Microcline
Gibbsite
Kaolinite
A
B
C
D
E
F

The reaction path first appears on figure 2 at point A in the gibbsite stability field. At point A, 0.02395061 μmols of K-spar have dissolved per kg of H_2O; the solution is just saturated with gibbsite, but no gibbsite has yet precipitated. With gibbsite as the second mineral in the MINERALS input, runs 5-7 show that the next stable phase boundary encountered is kaolinite and the net K-spar mass transfer from pure water to the gibbsite-kaolinite phase boundary (point B of fig. 2) is 2.173389 μmols/kg H_2O. In reaching the gibbsite-kaolinite phase boundary 1.957486 μmols of gibbsite were precipitated along the path from point A to B (fig. 2, run 5, table 18). Including gibbsite and kaolinite as second and third minerals in the MINERALS list, runs 8-9 show that the reaction path (to either the muscovite or microcline phase boundary) dissolves more gibbsite than was originally formed along path A-B (table 18). Therefore, the solution must react at equilibrium along the gibbsite-kaolinite phase boundary until the previously formed mass of gibbsite is exactly consumed. This point, where the gibbsite mass is zero and the solution is in equilibrium with gibbsite and kaolinite, is found in run 10 (cards 112-122, table 17), and located at point C on figure 2. Beyond point C, continued irreversible weathering of feldspar causes the solution to become increasingly undersaturated with gibbsite and because there is no more mass of gibbsite to dissolve, the path must enter the kaolinite stability field. The next phase boundary encountered is the kaolinite-muscovite boundary (run 11, point D) because the path to the kaolinite-microcline boundary (run 12) results in a metastable solution (table 18). Including kaolinite and muscovite in the MINERALS input, we find that the path to microcline equilibrium (run 13) dissolves more kaolinite than is present in the system at point D (9.435881 μmols/kg H_2O). Therefore, in run 14 we solve for the point along the kaolinite-muscovite phase boundary where the mass of kaolinite becomes zero (point E, fig. 2). As microcline continues to dissolve, the solution becomes increasingly undersaturated with both gibbsite and kaolinite until overall equilibrium is reached at the muscovite-microcline phase boundary (point F, run 15). The total mass of microcline dissolved to reach overall equilibrium is 181.5095 μmols/kg H_2O. At point F the masses of gibbsite and kaolinite are zero (in the beaker) and 60.49252 μmols of muscovite have formed per kg of water.

Part B. - <u>Paths across stability fields</u>.

Although the paths from A to B, C to D, and E to F across the gibbsite, kaolinite and muscovite stability fields are nearly linear in this problem (fig. 2), these paths are not <u>necessarily</u> linear. Part B is used to define the position of the reaction paths across the gibbsite, kaolinite and muscovite stability fields. The input cards for part B are listed in table 19. Cards 1-36 which apply to path A-B on figure 2 are identified as follows: Cards 1-25 (table 19) are essentially identical to cards 1-25 of table 17 used in part A to define the gibbsite saturated solution (point A on fig. 2). The only difference is that in part B (card 18, table 19) the gibbsite saturated solution is saved in solution 1 (IOPT(7) = 1). This defines the starting point (point A on fig. 2) for the irreversible reaction path to point B (fig. 2). The mass of microcline dissolved between points A and B is found by subtracting the net mass transfer to point A from the net mass transfer to point B as given in table 18 (2.173389 μmol - 0.02395061 μmol = 2.149438 μmol K-spar dissolved between points A and B). Cards 26-36 then run the reaction from point A to B by adding 2.149 μmols (rounded figure) of microcline to solution A in 5 equal steps while maintaining equilibrium with gibbsite. In particular note that on card 27 (table 19) IOPT(3) is 4 which indicates that a net reaction is added to solution 1 in NSTEPS steps. NSTEPS is 5, and there are 3 components in the reaction (REACTION) which defines microcline stoichiometry. The net mass transfer between A and B is given as STEPS input (card 32-33, table 19).

Similar calculations to define the path across the kaolinite stability field (cards 37-64) and across the muscovite stability field (cards 65-98) are also given in table 19. The results of part B are plotted on figure 2.

The reaction path calculations summarized above for part A were constructed to give net reaction from pure water to the desired phase boundary. An alternate method of calculation is to save each computed solution (IOPT(7) = 1) so that the mass transfer calculated to the next phase boundary is the net value between the two points. But either way, the results are the same.

Although we have solved this reaction path problem rigorously, the results of the calculation are limited by the constraints selected in its definition.

Table 19. - Card images of input data set for test problem 5, part B.

```
CARD NO.                               COLUMN

            10        20        30        40        50        60        70        80
    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

 1  TEST PROBLEM #5 PART B  DEFINE REACTION PATHS ACROSS STABILITY FIELDS.
 2  010000100  0 0
 3  SOLUTION 1
 4  PURE WATER
 5   0  0 0          7.0       4.0      25.0       1.0
 6  LOOK MIN
 7  GIBBSITE   3          0.0     8.049   -22.792     0
 8    10       1.0    3        3.0   1       -3.0
 9  KAOLINIT   4          0.0     5.708   -35.306     0
10    10       2.0    3        1.0  13        2.0   1       -6.0
11  MUSCOVIT   4          0.0     12.97   -59.377     0
12    10       3.0   13        3.0   7        1.0   1      -10.0
13  MICROCLN   5          0.0    0.875   -12.467     0
14    10       1.0   13        3.0   7        1.0   3       -4.0   1       -4.0
15
16  END
17  FIND AMOUNT OF K-SPAR DISSOLVED TO REACH GIBBSITE SATURATION.
18  0160001000 1 3
19  MINERALS
20  GIBBSITE   3          0.0     8.049   -22.792     0
21    10       1.0    3        3.0   1       -3.0
22
23  REACTION
24     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
25  END
26  PATH A TO B  (ACROSS GIBBSITE STABILITY FIELD) IN 5 EQUAL STEPS.
27  004000000  5 3
28  MINERALS
29  GIBBSITE   3          0.0     8.049   -22.792     0
30    10       1.0    3        3.0   1       -3.0
31
32  STEPS
33  .000002149
34  REACTION
35     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
36  END
37  DEFINE PURE WATER AS STARTING SOLUTION.
38  010000100  0 0
39  SOLUTION 1
40  PURE WATER
41   0  0 0          7.0       4.0      25.0       1.0
42  END
43  FIND AMOUNT OF K-SPAR DISSOLVED AS PATH ENTERS KAOLINITE STABILITY FIELD.
44  0160001000 1 3
45  MINERALS
46  GIBBSITE   3          0.0     8.049   -22.792     0
47    10       1.0    3        3.0   1       -3.0
48  KAOLINIT   4          0.0     5.708   -35.306     0
49    10       2.0    3        1.0  13        2.0   1       -6.0
50

    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'
            10        20        30        40        50        60        70        80
```

```
CARD NO.                              COLUMN

               1 0       2 0       3 0       4 0       5 0       6 0       7 0       8 0
    +++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'+++++++++'

51  REACTION
52     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
53  END
54  PATH C TO D (ACROSS KAOLINITE STABILITY FIELD) IN 5 EQUAL STEPS.
55  004000000  5 3
56  MINERALS
57  KAOLINIT   4          0.0     5.708   -35.306     0
58    10        2.0   3        1.0  13        2.0   1       -6.0
59
60  STEPS
61  .000016026
62  REACTION
63     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
64  END
65  DEFINE PURE WATER AS STARTING SOLUTION.
66  010000100  0 0
67  SOLUTION 1
68  PURE WATER
69   0  0 0          7.0       4.0      25.0       1.0
70  END
71  FIND AMOUNT OF K-SPAR DISSOLVED AS PATH ENTERS MUSCOVITE STABILITY FIELD.
72  0160001000 1 3
73  MINERALS
74  KAOLINIT   4          0.0     5.708   -35.306     0
75    10        2.0   3        1.0  13        2.0   1       -6.0
76  MUSCOVIT   4          0.0     12.97   -59.377     0
77    10        3.0  13        3.0    7        1.0   1      -10.0
78
79  REACTION
80     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
81  END
82  PATH E TO F (ACROSS MUSCOVITE STABILITY FIELD) IN 5 EQUAL STEPS.
83  004000000  5 3
84  MINERALS
85  MUSCOVIT   4          0.0     12.97   -59.377     0
86    10        3.0  13        3.0    7        1.0   1      -10.0
87
88  STEPS
89  .000150523
90  REACTION
91     7     1.0     0.0  10     1.0     0.0  13     3.0     0.0
92  END
```

HOW TO RUN PHREEQE ON THE USGS IBM AMDAHL COMPUTER

In order to run PHREEQE on the USGS Amdahl 470V/7 computer, the first card of the job must be a legitimate JOB card as defined in the Computer Center Division's user's manual.

```
//AA1yyyxx JOB ( . . . ),'user name',CLASS=x
```

The following JCL (Job Control Language) statements will execute the program PHREEQE:

```
//  EXEC FORTRUN,PROG=PHREEQE,REGION=180K,TIME=(0,15),COND=(11,LT),
//  ULIB='BFJONES.PGMLIB'
//FT10F001 DD DSN=PARK.DATA.PHREEQE,DISP=SHR

                    Insert input data deck here

//
$$$
```

The TIME parameter indicates the maximum run time for the program is 0 minutes and 15 seconds. The length of time for each run depends on the number of elements, the number of phases, and largely on the size of the change of redox potential which the program must calculate. In general redox problems run more slowly than non-redox problems. Usually less than one second is sufficient time to solve a single solution. Run times for the five test problems are summarized in Table 20 along with total lines printed and total iterations for each problem.

Table 20. - Job statistics for test problems

Test problem	Lines printed	Total iterations	Execution time, seconds
1	352	11	0.89
2 (A-D)	704	69	1.35
3	705	102	1.55
4 (A-E)	2091	257	3.44
5 (A)	1538	144	1.77
5 (B)	2183	167	1.88
TOTAL	7573	750	10.88

The user may wish to change the basic data file from PARK.DATA.PHREEQE to a data set of his own. In this case the DSN, UNIT, and VOL parameters for FT10F001 must be changed to correspond with the user's card image file.

The card input for the simulations to be run follow directly after the last JCL card (//FT10F001...). The first card of this input must be a title card (A.1 of input section) followed by an option card and other cards as described in the section, Description of Input.

A preliminary data set for PHREEQE is listed in Attachment A. These data are stored on the Amdahl in a catalogued, sequential data set named, PARK.DATA.PHREEQE. If the user wishes to use his own data set, the DSN parameter for file FT10F001 must be changed in the above JCL to correspond to the user's card-image data file.

The cards necessary to run test problems 1, 4A, and 4E are stored in a catalogued, sequential, card-image file named PARK.PHREEQE.CASES. It is possible to run these test cases directly from disk (without making a card deck) by inserting a new card after the JCL to run PHREEQE. Note that 190K of core is necessary to run the program in this way. The cards for the run stream would be as follows:

```
//  EXEC FORTRUN,PROG=PHREEQE,REGION=190K,TIME=(0,15),COND=(11,LT),
//  ULIB='BFJONES.PGMLIB'
//FT10F001 DD DSN=PARK.DATA.PHREEQE,DISP=SHR
//SYSIN DD DSN=PARK.PHREEQE.CASES,DISP=SHR
//
$$$
```

The Fortran source code listed in Attachment B is stored on the Amdahl in a catalogued, partitioned data set named BFJONES.CARDS. The member name is PHREEQE. Listings and punched cards can be obtained using the JCL for partitioned data sets given in Chapter 2 of the USGS Computer User's Manual. Listings and punched cards of the test cases (PARK.PHREEQE.CASES) and data base (PARK.DATA.PHREEQE) can be obtained by using the JCL for sequential data sets given in Chapter 2 of the USGS Computer User's Manual.

ADAPTATION OF FORTRAN CODE FOR COMPUTERS OTHER THAN THE AMDAHL COMPUTER

PHREEQE uses several non-standard IBM FORTRAN H extended enhancements to FORTRAN IV in an effort to conserve memory and shorten the card deck. If the source code is to be used on another computer, the non-standard features may have to be modified. This section only points out known problem areas and so is not necessarily complete. No attempt is made to give complete statement by statement modifications which might be necessary if problems occur.

FORTRAN H allows various word lengths for variables and PHREEQE uses the shortest word lengths which give the necessary precision for the numerical method. All integers are implicitly declared as 2 byte words, all variables beginning with the letter "D" are declared as double precision, "REAL*8" (17 - 18 decimal digits), and all other real numbers are implicitly single precision, "REAL*4" (7 decimal digits). Other "REAL*8" variables are declared explicitly at the beginning of each subroutine. Some computers may not allow the INTEGER*2 or the REAL*8 statements. Care should be taken to ensure there is no loss of precision when redefining the word length for REAL*8 variables. Function names for REAL*8 variables, absolute value (DABS) and minimum of two numbers (DMIN1) are not standard.

Another possible problem in compiling the code on another machine is the ENTRY statement. Two of PHREEQE's subroutines, PTOT and THORIT, are really collections of subroutines which use ENTRY statements instead of SUBROUTINE statements. The only advantage to this is that common blocks and declaration statements do not have to be repeated for each subroutine. Each computer handles entry points differently and some do not allow argument lists in the ENTRY statement. In most cases, making each entry point a separate subroutine with all the common blocks and declarations will eliminate any problems. In making each entry print into a subroutine, a call to PSUM must be inserted at the end of PSPEC. ENTRY RDATA, however, can not be easily separated from subroutine READ. The logic of the entry point must be maintained in rewriting this entry point (perhaps with a call to READ instead of RDATA and a jump to the point where the ENTRY statement is in the code).

Subroutine CHECK returns to three different points in subroutine MODEL by using a RETURN n statement. This statement may have a different form or may be illegal on another computer.

The program assumes there is a file, labeled in the Fortran Code as 10, from which it will read the basic thermodynamic data. If no file exists then the call to entry RDATA must be removed from the main program and all data must be read with the rest of the input data stream (file 5, or the card reader).

DESCRIPTION OF SUBROUTINES

A complete listing of the FORTRAN code for PHREEQE is found in Attachment B. The following text describes the functions of each subroutine in the order in which they are found in the code.

MAIN contains the logic of the program in its sequence of calls to other subroutines. It calls subroutines which read the data, solve the initial solution(s), and simulate the reactions. The process is repeated until the end of the input data at which time the program terminates in subroutine READ.

Subroutine READ along with its entry point, RDATA, is the only means of entering data into the program. RDATA is called once at the beginning of a job and reads the basic aqueous model data off a disk file (10). RDATA reads a card image file composed of keyword data blocks identical to those described in the input section of this paper. Generally SPECIES, ELEMENTS, and LOOK MIN data blocks would be placed on the disk because they are subject to few changes and are lengthy card decks. RDATA prints the statement, "DATA READ FROM DISK" followed by a list of the keywords encountered while processing the disk file. Subroutine READ processes the input data deck one simulation at a time. First a title card and an option card are read and then the remainder of the input for a simulation is processed on a keyword basis. A keyword is read and the data following are processed, then another keyword is read and so on until the keyword END indicates the end of a simulation's input. Each card is printed as it is read although the printed output may not be identical to the input cards since most of the data are processed as numbers rather than alphanumeric characters. The program terminates in this subroutine if an end of file is read or if any of the data necessary for the specified options are missing. In the latter case an error message is printed, "TERMINAL ERROR INPUT LACKED (keyword) CARDS".

Subroutine MINCON rewrites all input mineral reactions in terms of master species. If Fe^{2+}, SO_4^{2-}, H_2O, H^+, and e^- are master species and the following mineral reaction is entered:

$$FeS = Fe^{2+} + S^{2-}$$

then S^{2-} would be converted to the master species according to the association reaction for the aqueous species S^{2-},

$$SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O \ .$$

The mineral dissociation reactions actually used by the program will be:

$$FeS + 4H_2O \quad = \quad Fe^{2+} + SO_4^{\;2-} + 8H^+ + 8e^-$$

$$\log K \quad = \quad \log K_{input} - \log K_{S^{2-}} \; .$$

A list is made (in array LMCON) of all the association reaction log K's which must be subtracted from the input Log K. In this way analytical and Van't Hoff expressions can be correctly combined to calculate the log K of the mineral at a new temperature.

Subroutine INOUT chooses which elements and species from the data base are to be included in the aqueous model for a given calculation. Only elements with total concentrations greater than zero are marked "present" and only those species containing only "present" elements are included. This routine also zeros the array, AR, and puts the mineral coefficients (they remain unchanged through the reaction) into the array.

Subroutine PICK1 determines the position of the electrical balance and the mass balance equations in array AS. This subroutine is used only for the initial solution problem.

Three error conditions are also checked in this subroutine, each of which will cause termination of the program if detected. If alkalinity was specified but no positive total alkalinity was input, then the following is printed, "CARBON WAS SPECIFIED AS ALKALINITY BUT WAS LESS THAN OR EQUAL TO 0.0. CALCULATIONS TERMINATED."

If the same species is chosen for the alkalinity and the NEUTRAL species then this message is output, "ALKALINITY SPECIES CAN NOT BE THE SAME AS THE NEUTRAL SPECIES. CALCULATIONS TERMINATED."

Finally, if alkalinity is input and pH is chosen for the electrical balance option, the following is printed, "IT IS THEORETICALLY IMPOSSIBLE TO FIX THE ALKALINITY AND STILL FIND ELECTRICAL NEUTRALITY BY ADJUSTING pH. IF ALKALINITY IS TO BE INPUT IOPT(2) CAN NOT BE EQUAL TO 1."

Entry PICK2 determines the row numbers for the equations in array AS during the reaction steps of a simulation.

PICK2 also adds small amounts of minerals to the solution if an element is contained in a mineral but does not have a positive concentration in the solution. The procedure is complicated by the possibility of negative coefficients for elements in minerals. If the algorithum fails to produce positive concentrations for all the appropriate elements then the following message is printed, "I HAD TROUBLE ADDING MINERALS SO THAT ALL THE NECESSARY ELEMENTS HAD POSITIVE CONCENTRATIONS. PLEASE ADJUST INITIAL CONCENTRATIONS TO SOME SMALL POSITIVE QUANTITY."

Subroutine KTEMP calculates the association constants for the aqueous species and the equilibrium constants for the mineral phases. Either an analytical expression or a Van't Hoff expression is used.

Subroutine STEP recalculates the total concentration of elements in solution for a reaction step. In addition, any temperature change for the reaction step is set in this subroutine.

Subroutine SET makes initial estimates of the activities of the master species.

Subroutine MODEL iteratively calls other subroutines which provide approximations to the solution of the problem. The program exits from MODEL when the calculations have converged within specified limits.

Subroutine GAMMA calculates the activity of water, the ionic strength of the solution, and the activity coefficients for each species using one of the following formulas:

1. Extended Debye-Hückel,
2. WATEQ Debye-Hückel,
3. Davies equation.

Subroutine AQMOD is one the most critical subroutines of the program. It was written with an emphasis on convergence at the expense of computing speed. The scheme employed in this subroutine is as follows:

1. Calculate molalities from new activity coefficients (subroutine GAMMA) and old activities of master species.

2. Revise activities for cation master species to improve mass balance for cations.

3. Calculate molalities from activity coefficients and revised activities of master species.

4. Revise activities for anion and neutral master species.

5. Calculate molalities from activity coefficients and revised activities of master species.

6. Fill in array AR (linearization of nonlinear equations.)

7. In Entry SI, calculate inverse saturation index for minerals.

The subroutine uses the following method to revise master species' activities:

$$a_{j,new} = a_{j,old} \cdot \frac{\text{Total concentration}}{\sum_{i=1}^{I} m_i \cdot c_{i,j}} .$$

If there is a large fraction of an element in a species involving the square or higher power of the master species (e.g. N_2 when NO_3^- is the master species) then a quadratic formulation is used,

$$a_{j,new} = a_{j,old} \cdot \frac{- B + \sqrt{B**2 + 4 A C}}{2A}$$

where,

B = sum of the molalities of species with the master species raised to the first power,

A = sum of the molality of the element in species in which the master species is raised to a power greater than one, and

C = total molality of the element.

Subroutine CHECK tests for convergence to the solution of the equations. If the errors are less than specified tolerences (less than 1 in the sixth significant digit) the problem is solved. If the solution has not converged then another iteration is begun. If mass balance is not satisfied within 20 percent (a smaller tolerence is substituted as the iterations increase) or the ionic strength is changing rapidly then the matrix is not solved and only mass balance is considered for the next iteration.

If the number of iterations for a single simulation exceeds 200 then the calculations are terminated and the following message is printed, "CALCULATIONS TERMINATED AT 200 ITERATIONS."

The numbers used in the convergence criteria are contained in a data statement in the code for this subroutine. These numbers seem to work well. Relaxing the criteria may make the program run faster, however, experience has shown that the last few orders of magnitude in accuracy require few iterations. This indicates any time savings would be marginal.

Subroutine SOLVE copies the matrix coefficients from array AR to array AS. Only the rows and columns of the necessary equations are copied. Finally, the matrix solving routine SLNQ is called.

Subroutine RESET calculates 1) a new pH, 2) a new pe, 3) the moles of minerals to dissolve or precipitate, and 4) the new total concentrations of the elements. Several modifications are made to the DELTA vector derived from SLNQ, the linear equation solver. Significant operations in this subroutine are as follows:

1. $\frac{\Delta a_{H^+}}{a_{H^+}}$ and $\frac{\Delta a_{e^-}}{a_{e^-}}$ must be between 1.5 and -.75. If scaling is necessary, both values are adjusted by the same factor, preserving the ratio of the DELTA values.

2. The DELTA values for the minerals are scaled only to avoid a negative total concentration of an element. In this case all DELTA values for the minerals are reduced by the same factor.

3. No total concentration of an element is allowed to drop below 10^{-30}. This is necessary to prevent underflows in computing.

The subroutine keeps a cumulative sum of the total amount of each mineral phase which has been added or removed from the aqueous phase.

Subroutine THORIT is a collection of utility subroutines. Entry THORIT calculates the oxidation state of the solution by summing the OPV (operational valence) of each of the aqueous species.

Entry SOLN transfers a set of total concentrations from the storage array TOTAL to the active array TOT. TOT is used in solving any problem.

Entry SAVE transfers a set of totals from the active array TOT to the storage array TOTAL. This is the reverse process of Entry SOLN.

Entry ZEROAR sets the active portions of the array AR to zero. This routine is called between iterations.

Entry CHKSPE checks each species input to insure all reactions are written in terms of master species (master species have index numbers less than 30). If a species fails this test a message is printed, "SPECIES HAS A MASTER SPECIES NUMBER OUT OF RANGE". A second test of the species reaction input is also performed in this entry point which insures that the reaction is charge balanced. Lack of charge balance results in a terminal error with the message, "***** ERROR IN SPECIES NUMBER (number) (name) REACTION DOES NOT CHARGE BALANCE."

Entry CHKMIN sums the charge of the species in the mineral reaction to make sure they sum to zero and also sums the OPV state of the species to ensure that it equals the OPV state of the mineral. The error messages are respectively: "***** ERROR IN MINERAL (number) (name) REACTION DOES NOT CHARGE BALANCE." and "***** ERROR IN MINERAL (number) (name) REACTION DOES NOT BALANCE THE SPECIFIED VALENCE."

Entry CHKLK performs a charge balance check on the look minerals. An error in the look minerals is not fatal but produces a warning, "***** WARNING: LOOK MINERAL NUMBER (number) (name) REACTION DOES NOT CHARGE BALANCE."

Entry UNITS converts the total concentration of the elements from the units in which they were input to molality. IUNITS indicates the input units, 1 = mmoles/l; 2 = mg/l; 3 = ppm; and 0 = molality. If IUNITS = 2 or 3, and the sum of the weights of solute is greater than a kilogram then the following message is printed, "TERMINAL ERROR TOTAL SALT PPM GREATER THAN 1 MILLION. CHECK CONCENTRATION UNITS AND ELEMENT GRAM FORMULA WEIGHT INPUT".

Function UNDER exponentiates the log of the molality of a species. Molalities of less than 10^{-35} are set to zero. Molalities greater than 10^5 (intermediate calculations) are set to 10^5. This function is necessary to prevent underflows.

Subroutine PTOT is a collection of print subroutines. PTOT prints total molalities of the elements. Entry PSPEC prints the activities, molalities, and activity coefficients for the aqueous species included in the problem. Entry PSUM calculates and prints any sums of molalities of species requested by the input deck.

Entry PBUG provides a long printout which is helpful only in debugging a nonconvergent problem. A number called the reduction factor followed by eight columns of numbers is output. The reduction factor is the scaling factor by which SLNQ DELTAs were multiplied to produce the fourth column of output. The columns of output from this routine are as follows:

1. Error in an equation (difference from mass balance for an element or inverse saturation index for a mineral),

2. Element or mineral name,

3. Calculated delta in total concentration or delta (moles) for minerals,

4. Ratio of change in concentration to total concentration,

5. Master species name,

6. Activity of master species,

7. Always zero except when using a species other than H^+ to achieve electrical neutrality. In that case, column 7 is the change in activity of the neutrality species.

8. Also zero with the same exception as column 7. It contains the ratio of the change in the activity of the neutrality species to the activity of the species.

Entry PPHASE in subroutine PTOT prints the mass transfer and saturation index for each mineral included in a reaction simulation. Mass transfer is not cumulative over a series of reaction steps. PLOOK prints saturation indices for the minerals specified by LOOK MIN input. PDATA reads the data file (file 10) and prints the card images.

Subroutine SLNQ solves a system of linear equations, using Gaussian elimination. The common block of SLNQ is modified to accomodate the variable names A and X for the matrix AS and solution vector DELTA. If the matrix is found to be singluar, an error message is printed and the program terminates. The message is, "THE GIBBS PHASE RULE HAS BEEN VIOLATED". If IOPT(9) = 1, then the rows of the array to be solved are printed each time the subroutine is called.

Table 21. - List of major variables 1/

A	Constant parameter in extended Debye-Hückel activity coefficient expression.
ADHSP	Parameters for WATEQ Debye-Hückel expression. (2)
ALKSP	Alkalinity contribution for each species (meq/mole). (1)
ALOOK	Analytical expression, as a function of temperature, for equilibrium constant of Look Minerals. (2)
AMIN	Analytical expression, as a function of temperature, for equilibrium constant of Minerals. (1)
AR	Primary array. Rows and columns for each of the following: 1. electrical balance equation, 2. electron balance equation, 3. 27 element mass balance equations, 4. 20 mineral equilibrium equations. (2)
AS	Secondary array. Only the essential rows and columns of AR are copied into AS. (2)
ASP	Analytical expressions, as a function of temperature, for association constants for aqueous species. (2)
B	Constant parameter in Debye-Hückel expression.
CLOOK	Stoichiometric coefficients for Look Minerals. (2)
CMCON	Stoichiometric coefficients for reactions necessary to convert input dissociation reaction constant to dissociation constant in terms of master species for Look Minerals. (2)
CMIN	Stoichiometric coefficients for Minerals in terms of master species. (2)
CMINO	Input stoichiometric coefficients for Minerals (not necessarily master species.) (2)
CR	Array of errors in equations. (1)
CREAC	Stoichiometric coefficients for reaction. (1)
CS	Copy of CR with only essential rows. (1)

Table 21. - List of major variables (cont'd.)

CSP	Stoichiometric coefficients for aqueous species in terms of association to master species. (2)
DALKS	Alkalinity calculated from distribution of species in solution.
DALKT	Total input alkalinity.
DELTA	Solution to set of linear equations AS. (1)
DELTOT	Change in total concentration of elements calculated from DELTA values for minerals. (1)
DHA	Ion size parameter for Debye-Hückel expression. (1)
DHLOOK	ΔH_r^o in Van't Hoff expression for Look Mineral dissociation equilibrium constants. (1)
DHMIN	ΔH_r^o in Van't Hoff expression for Mineral dissociation equilibrium constants. (1)
DHSP	ΔH_r^o in Van't Hoff expression for aqueous association reactions. (1)
DIFFZ	Electrical imbalance of the initial solutions. (1)
DZOFF	Electrical imbalance from initial solutions to be maintained in current calculations. (1)
DNEUT	Total for neutrality species before calculations.
ELECT	Charge difference between the sum of the anions and the sum of the cations.
GFLAG	Option flag for method of calculating activity coefficients. (1)
GFW	Gram formula weight of master species of elements. (1)
HEAD	Title card for input solutions. (2)
IALK	Flag to indicate whether total carbon or alkalinity was entered. (1)
IASPEC	Master species number of carbon.

Table 21. - List of major variables (cont'd.)

IESPEC	Number of the species to be used to adjust the electrical balance.
IFE	Row of the electrical balance equation in AS.
IFM	Row of the first mineral equation in AS.
IFT	Row of the first mass balance equation in AS.
IFTH	Row of the electron balance equation in AS.
IIN	Array indicating which rows of AR are to be considered. (1)
ILE	Same as IFE.
ILM	Row of last mineral equation.
ILT	Row of last mass balance equation.
ILTH	Same as IFTH.
IOPT	Array of input options. (1)
IOUT	Array with row number of AR corresponding to each row of AS. (1)
ISOL	Number of the solution being solved.
ISOLV	Flag to indicate if a new solution has been read for this simulation. (1)
ISTEP	Number of the current reaction step.
ITER	Counter for the number of iterations in a step.
IUNITS	Flag to indicate concentration units of input. (1)
KFLAG	Flag to indicate whether analytic or Van't Hoff expression is used for calculating association constants of aqueous species. (1)
LA	Log of the activity (array filled for master species only). (1)
LASTS	Number of last aqueous species used in simulation.

Table 21. - List of major variables (cont'd.)

LASTT	Number of last element used in simulation.
LG	Log of activity coefficient. (1)
LKLOOK	Log of equilibrium constant for Look Minerals for the reaction written in terms of master species. (1)
LKMIN	Log of equilibrium constant for Minerals written in terms of master species. (1)
LKMINO	Log of equilibrium constant for Minerals written in terms of input species. (1)
LKOLK	Log of equilibrium constant for Look Minerals in terms of input species. (1)
LKSP	Log of association constant for aqueous species. (1)
LKTOM	Log of equilibrium constant of Minerals at 25°C for use in the Van't Hoff expression. (1)
LKTOSP	Log of association constant of aqueous species at 25°C for use in the Van't Hoff expression. (1)
LLOOK	List of species numbers in Look Minerals. (2)
LM	Log of molality of aqueous species. (1)
LMCON	List of species numbers to convert Mineral equilibrium constants from input species to master species. (2)
LMIN	List of master species numbers in Minerals. (2)
LMINO	List of input species numbers in Minerals. (2)
LNEG	Index number of negatively charged master species to be used to adjust electrical neutrality.
LOOKFL	Flag to indicate type of expression used to calculate equilibrium constants for Look Minerals. (1)
LPOS	Index number of positively charged master species to be used to adjust electrical neutrality.
LREAC	List of species numbers to be used in adding a net stoichiometric reaction. (1)

Table 21. - List of major variables (cont'd.)

LSP	List of master species numbers to form aqueous species. (2)
LSUM	List of species numbers to be summed and printed on output. (2)
M	Molality of aqueous species. (1)
MAXEQ	Maximum number of equations.
MAXM	Maximum number of Minerals.
MAXS	Maximum number of Species.
MAXT	Maximum species number of a master species.
MAXT1	MAXT + 1.
MFLAG	Flag to indicate which expression to use to calculate Mineral equilibrium constants. (1)
MNAME	Alphanumeric name of Minerals. (1)
MU	Ionic strength of the solution.
NAMELK	Alphanumeric name of Look Minerals. (1)
NCOMPS	Number of constituent species in the stoichiometric reaction.
NELTS	In common blocks but not used.
NEQ	Total number of equations in the simulation.
NEQ1	NEQ + 1.
NLOOK	Number of species in Look Minerals. (1)
NLOOKS	Number of Look Minerals.
NMCON	Number of reactions necessary to convert input equilibrium constants to master species equilibrium constants for Minerals. (2)
NMIN	Number of master species in Minerals. (1)
NMINO	Number of input species in Minerals. (1)

Table 21. - List of major variables (cont'd.)

NMINS	Number of Minerals in the simulation.
NRMINS	Number of Minerals to be considered in the reaction steps.
NSP	Number of master species in an aqueous species. (2)
NSPECS	Not used.
NSTEPS	Number of reaction steps to be taken.
NSUM	Number of species in a Sum for display. (1)
NSUMS	Number of Sums to be displayed.
PE	Negative log of the activity of the electron.
PH	Negative log of the activity of the hydrogen ion.
SDENS	Density of initial solutions. (1)
SFLAG	Flag to indicate the type of expression (Van't Hoff or analytical) to be used for the association constant of aqueous species. (1)
SNAME	Alphanumeric name of aqueous species. (1)
SUNAME	Alphanumeric name to be printed with Sums. (1)
TC	Temperature in degrees Celsius.
TEMP	Temperature, in degrees Celsius, stored for each solution. (1)
TH	Value of OPV (operational valence) of each saved solution. (1)
THMEAN	Mean OPV of an element added in a stoichiometric reaction. (1)
THMIN	OPV of a Mineral. (1)
THOR	Absolute OPV of a solution.
THREAC	Net OPV of a stoichiometric reaction.
THSOLN	OPV of a solution determined by the distribution of aqueous species during iterations.
THSP	OPV of the aqueous species. (1)

Title 21. - List of major variables (cont'd.)

TITLE	Alphanumeric heading for a simulation. (1)
TITRML	Not used. (1)
TITRPH	Not used. (1)
TK	Temperature in degrees Kelvin.
TNAME	Alphanumeric name of elements. (1)
TOT	Total concentration of elements in solution. (1)
TOTAL	Stored values of total concentrations for each solution. (2)
TSTEP	Temperature for each reaction step. (2)
VO	Initial volume of Solution 1 in a titration reaction.
XSTEP	Amount of reaction for each reaction step. (2)

---

[1] Number in parentheses indicates the number of subscripts associated with each variable.

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Attachment A. - Preliminary thermodynamic data base for PHREEQE

```
ELEMENTS
Ca          4   40.08          CA+2
Mg          5   24.305         MG+2
Na          6   22.9898        NA+
K           7   39.0983        K+
Fe          8   55.847         FE+2
Mn          9   54.9380        MN+2
Al         10   26.9815        AL+3
Ba         11   137.33         BA+2
Sr         12   87.62          SR+2
Si         13   60.0843        SIO2
Cl         14   35.453         CL-
C          15   44.0098        CO2
S          16   96.06          SO4-2
N          17   62.0049        NO3-
B          18   10.81          B
P          19   94.9714        PO4-3
F          20   18.9984        F-
Li         21    6.941         LI+
Br         22    79.904        BR-

SPECIES
  1
H+          101 1.0       0.0       9.0       9.0                 0.0
 0.0        0.0
  1 1.0
  2
E-          100 -1.0      0.0       0.0                           0.0
 0.0        0.0
  2 1.0
  3
H2O         100 0.0       0.0       0.0                           0.0
 0.0        0.0
  3 1.0
  4
Ca+2        101 2.0       0.0       6.0       5.0       0.165     0.0
 0.0        0.0
  4 1.0
  5
Mg+2        101 2.0       0.0       8.0       5.5       0.20      0.0
0.0        0.0
  5 1.0
  6
Na+         101 1.0       0.0       4.0       4.0       0.075     0.0
0.0        0.0
  6 1.0
  7
K+          101 1.0       0.0       3.0       3.5       0.015     0.0
0.0        0.0
  7 1.0
  8
Fe+2        100 2.0       2.0       6.0                           0.0
0.0        0.0
  8 1.0
  9
Mn+2        100 2.0       2.0       6.0                           0.0
 0.0        0.0
```

```
  9 1.0
 10
Al+3        100 3.0   0.0       9.0                           0.0
 0.0       0.0
 10 1.0
 11
Ba+2        100 2.0   0.0       5.0                           0.0
 0.0       0.0
 11 1.0
 12
Sr+2        101 2.0   0.0       5.0       5.26      0.121     0.0
 0.0       0.0
 12 1.0
 13
H4SiO4      100 0.0   0.0       0.0                           0.0
 0.0       0.0
 13 1.0
 14
Cl-         101 -1.0  0.0       3.0       3.5       0.015     0.0
 0.0       0.0
 14 1.0
 15
CO3-2       101 -2.0  4.0       4.5       5.4       0.0       2.0
 0.0       0.0
 15 1.0
 16
SO4-2       101 -2.0  6.0       4.0       5.0       -0.04     0.0
 0.0       0.0
 16 1.0
 17
NO3-        100 -1.0  5.0       3.0                           0.0
 0.0       0.0
 17 1.0
 18
H3BO3       100 0.0   0.0       0.0                           0.0
0.0       0.0
 18 1.0
 19
PO4-3       100 -3.0  0.0       4.0                           2.0
 0.0       0.0
 19 1.0
 20
F-          100 -1.0  0.0       3.5                           0.0
 0.0       0.0
 20 1.0
 21
Li+         100 1.0   0.0       6.0                           0.0
0.0       0.0
 21 1.0
 22
Br-         100 -1.0  0.0       3.0                           0.0
0.0       0.0
 22 1.0
 31
OH-         210 -1.0  0.0       3.5                           1.0
-14.000   13.362    -283.9710   -0.05069842 13323.0     102.24447   -1119669.0
  3 1.0     1 -1.0
 32
O2 AQ       300 0.0   4.0       0.0                           0.0
```

```
-86.08    134.79
  3 2.0     1 -4.0    2 -4.0
 33
H2 AQ       200 0.0       -2.0      0.0                           0.0
-3.15     -1.759
  1 2.0     2 2.0
 34
HCO3-       211 -1.0      4.0       4.5       5.4       0.0       1.0
 10.329    -3.561    107.8871    0.03252849  -5151.79    -38.92561  563713.9
 15 1.0     1 1.0
 35
H2CO3       310 0.0       4.0       0.0                           0.0
 16.681    -5.738    464.1965    0.09344813  -26986.16   -165.75951  2248628.9
 15 1.0     1 2.0     3 -1.0
 36
CH4 AQ      400 0.0       -4.0      0.0                           0.0
 41.071    -61.039
 15 1.0     1 10.0    2 8.0     3 -3.0
 40
HSO4-       210 -1.0      6.0       0.0                           0.0
 1.988      3.85      -56.889    0.006473    2307.9      19.8858
 16 1.0     1 1.0
 41
S-2         400 -2.0      -2.0      5.0                           2.0
 20.735     -28.04
 16 1.0     1 8.0     2 8.0     3 -4.0
 42
HS-         400 -1.0      -2.0      3.5                           1.0
 33.652    -40.14
 16 1.0     1 9.0     2 8.0     3 -4.0
 43
H2S         400 0.0       -2.0      0.0                           0.0
 40.644    -65.44
 16 1.0     1 10.0    2 8.0     3 -4.0
 48
NO2-        400 -1.0      3.0       3.0                           0.0
 28.57     -43.76
 17 1.0     1 2.0     2 2.0     3 -1.0
 49
N2 AQ       400 0.0       0.0       0.0                           0.0
 207.08    -312.13
 17 2.0     1 12.0    2 10.0    3 -6.0
 50
NH3 AQ      400 0.0       -3.0      0.0                           1.0
 109.83    -174.58
 17 1.0     1 9.0     2 8.0     3 -3.0
 51
NH4+        400 1.0       -3.0      2.5                           0.0
 119.077   -187.055
 17 1.0     1 10.0    2 8.0     3 -3.0
 52
NH4SO4-     500 -1.0      3.0       0.0                           0.0
 120.19    -187.055
 17 1.0     1 10.0    2 8.0    16 1.0     3 -3.0
 57
H2BO3-      200 -1.0      0.0       0.0                           1.0
-9.240     3.224
 18 1.0     1 -1.0
 58
```

```
BFOH3-      200 -1.0      0.0       0.0                                    0.0
-0.40      1.85
 18 1.0    20 1.0
 59
BF2OH2-     400 -1.0      0.0       0.0                                    0.0
7.628      1.635
 18 1.0    20 2.0     1 1.0     3 -1.0
 60
BF3OH-      400 -1.0      0.0       0.0                                    0.0
13.666     -1.58
 18 1.0     1 2.0    20 3.0     3 -2.0
 61
BF4-        400 -1.0      0.0       0.0                                    0.0
20.274     -1.795
 18 1.0     1 3.0    20 4.0     3 -3.0
 65
HPO4-2      200 -2.0      0.0       4.0                                    1.0
 12.346     -3.53
 19 1.0     1 1.0
 66
H2PO4-      200 -1.0      0.0       4.5                                    0.0
 19.553     -4.52
 19 1.0     1 2.0
 69
HF AQ       210 0.0       0.0       0.0                                    0.0
 3.18       3.18      -2.033     0.012645    429.01
  1 1.0     20 1.0
 70
HF2-        200 -1.0      0.0       0.0                                    0.0
 3.76       4.55
  1 1.0     20 2.0
 75
CaOH+       300 1.0       0.0       0.0                                    1.0
 -12.78
  4 1.0     3 1.0      1 -1.0
 76
CaCO3       210 0.0       4.0       0.0                                    2.0
3.224      3.545     -1228.732   -0.299440    35512.75     485.818
  4 1.0    15 1.0
 77
CaHCO3+     311 1.0       4.0       0.0        5.4         0.0        1.0
11.435     -0.871     1317.0071   0.34546894  -39916.84   -517.70761  563713.9
  4 1.0    15 1.0      1 1.0
 78
CaSO4       200 0.0       6.0       0.0                                    0.0
2.30       1.65
  4 1.0    16 1.0
 80
CaPO4-      200 -1.0      0.0       0.0                                    2.0
6.459      3.100
  4 1.0    19 1.0
 81
CaHPO4      300 0.0       0.0       0.0                                    1.0
15.085     -0.230
  4 1.0     1 1.0    19 1.0
 82
CaH2PO4+    300 1.0       0.0       0.0                                    0.0
20.961     -1.120
  4 1.0     1 2.0    19 1.0
```

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 83
CaF+        200 1.0       0.0       0.0                             0.0
0.940     4.12
  4 1.0    20 1.0
 85
MgOH+       300 1.0       0.0       0.0                             1.0
-11.44
  5 1.0     3 1.0     1 -1.0
 86
MgCO3       210 0.0       4.0       0.0                             2.0
2.98      2.713     0.9910     0.00667
  5 1.0    15 1.0
 87
MgHCO3+     310 1.0       4.0       0.0                             1.0
11.399    -2.771    48.6721    0.03252849  -2614.335     -18.00263  563713.9
  5 1.0     1 1.0    15 1.0
 88
MgSO4       200 0.0       6.0       0.0                             0.0
2.37      4.55
  5 1.0    16 1.0
 89
MgPO4-      200 -1.0      0.0       0.0                             2.0
6.589     3.100
  5 1.0    19 1.0
 90
MgHPO4      300 0.0       0.0       0.0                             1.0
15.216    -0.230
  5 1.0     1 1.0    19 1.0
 91
MgH2PO4+    300 1.0       0.0       0.0                             0.0
21.066    -1.120
  5 1.0     1 2.0    19 1.0
 92
MgF+        200 1.0       0.0       0.0                             0.0
1.82      3.2
  5 1.0    20 1.0
 93
NaOH        300 0.0       0.0       0.0                             1.0
 -14.18   0.0
  6 1.0     3 1.0     1 -1.0
 94
NaCO3-      200 -1.0      4.0       0.0                             2.0
1.27      8.91
  6 1.0    15 1.0
 95
NaHCO3      300 0.0       4.0       0.0                             1.0
10.079
  6 1.0     1 1.0    15 1.0
 96
NaSO4-      200 -1.0      6.0       0.0                             0.0
0.70      1.12
  6 1.0    16 1.0
 97
NaHPO4-     300 -1.0      0.0       0.0                             1.0
12.636    -3.530
  6 1.0     1 1.0    19 1.0
 98
NaF aq      200 0.0       0.0       0.0                             0.0
 -0.24
```

```
  6 1.0    20 1.0
 99
KOH         300 0.0       0.0       0.0                           1.0
 -14.46   0.0
  7 1.0     3 1.0     1 -1.0
100
KSO4-       200 -1.0      6.0       0.0                           0.0
0.85      2.25
  7 1.0    16 1.0
101
KHPO4-      300 -1.0      0.0       0.0                           1.0
12.636    -3.530
  7 1.0     1 1.0    19 1.0
102
FeOH+       300 1.0       2.0       0.0                           1.0
-9.500    13.2
  8 1.0     3 1.0     1 -1.0
105
FeCl+       200 1.0       2.0       0.0                           0.0
 0.14
  8 1.0    14 1.0
106
FeCO3       200 0.0       6.0       0.0                           0.0
4.38
  8 1.0    15 1.0
107
FeHCO3+     300 1.0       6.0       0.0                           0.0
 12.329
  8 1.0    15 1.0     1 1.0
108
FeSO4       200 0.0       8.0       0.0                           0.0
2.25      3.23
  8 1.0    16 1.0
109
FeHSO4+     300 1.0       +8.0
3.068
  8 1.0    16  1.0    1  1.0
110
Fe(HS)2     500 0.0       -2.0      0.0                           2.0
76.250    -120.280
  8 1.0    16 2.0     1 18.0    2 16.0    3 -8.0
111
Fe(HS)3-    500 -1.0      -4.0      0.0                           3.0
111.937   -180.420
  8 1.0    16 3.0     1 27.0    2 24.0    3 -12.0
112
FeHPO4      300 0.0       2.0       0.0                           1.0
15.946    -3.530
  8 1.0     1 1.0    19 1.0
113
FeH2PO4+    300 1.0       2.0       0.0                           0.0
22.253    -4.520
  8 1.0     1 2.0    19 1.0
114
FeF+        200 1.0       2.0       0.0                           0.0
 1.0
  8 1.0    20 1.0
115
Fe+3        200 3.0       3.0       9.0                           0.0
```

```
-13.02     9.68
  8 1.0     2 -1.0
117
FeOH+2      400 2.0       3.0       0.0                           0.0
-15.21    20.08
  8 1.0     3 1.0     2 -1.0    1 -1.0
118
FeOH2+      400 1.0       3.0       0.0                           0.0
-18.69    26.78
  8 1.0     3 2.0     1 -2.0    2 -1.0
119
FeOH3       400 0.0       3.0       0.0                           1.0
-25.58    34.48
  8 1.0     3 3.0     1 -3.0    2 -1.0
120
FeOH4-      400 -1.0      3.0       0.0                           2.0
-34.62    41.58
  8 1.0     3 4.0     1 -4.0    2 -1.0
121
Fe2OH2+4    400 4.0       6.0       0.0                           0.0
-28.99    32.86
  8 2.0     3 2.0     1 -2.0    2 -2.0
122
Fe3OH4+5    400 5.0       9.0       0.0                           0.0
-45.36    43.34
  8 3.0     3 4.0     1 -4.0    2 -3.0
123
FeCl+2      300 2.0       3.0       0.0                           0.0
-11.54    15.28
  8 1.0    14 1.0     2 -1.0
124
FeCl2+      300 1.0       3.0       0.0                           0.0
-10.89    10.0
  8 1.0    14 2.0     2 -1.0
125
FeCl3       300 0.0       3.0       0.0                           0.0
-11.89    10.0
  8 1.0    14 3.0     2 -1.0
126
FeSO4+      300 1.0       9.0       0.0                           0.0
-8.98     13.59
  8 1.0    16 1.0     2 -1.0
127
FeHSO4+2    400 2.0       +9.0
-8.552
  8 1.0    16  1.0    1  1.0    2  -1.0
128
FeSO42-     300 -1.0      15.0      0.0                           0.0
-7.64     14.28
  8 1.0    16 2.0     2 -1.0
129
FeHPO4+     400 1.0       3.0       0.0                           1.0
 4.74     12.23
  8 1.0     1 1.0    19 1.0     2 -1.0
130
FeH2P+2     400 2.0       3.0       0.0                           0.0
 11.95    5.48
  8 1.0     1 2.0    19 1.0     2 -1.0
131
```

```
FeF+2        300 2.0       3.0       0.0                              0.0
-6.82      12.38
  8 1.0     20 1.0     2 -1.0
132
FeF2+        300 1.0       3.0       0.0                              0.0
-2.22      14.48
  8 1.0     20 2.0     2 -1.0
133
FeF3         300 0.0       3.0       0.0                              0.0
0.98       15.08
  8 1.0     20 3.0     2 -1.0
134
MnOH+        300 1.0       2.0       0.0                              1.0
-10.59     14.40
  9 1.0      3 1.0     1 -1.0
136
MnCl+        200 1.0       2.0       0.0                              0.0
 0.61       0.0
  9 1.0     14 1.0
137
MnCl2        200 0.0       2.0       0.0                              0.0
 0.25       0.0
  9 1.0     14 2.0
138
MnCl3-       200 -1.0      2.0       0.0                              0.0
 -0.31      0.0
  9 1.0     14 3.0
139
MnCO3        200 0.0       6.0       0.0                              0.0
4.90
  9 1.0     15 1.0
140
MnHCO3+      300 1.0       6.0       0.0                              1.0
 12.279     0.0
  9 1.0     15 1.0     1 1.0
141
MnSO4        200 0.0       8.0       0.0                              0.0
 2.25      3.37
  9 1.0     16 1.0
142
Mn(NO3)2     200 0.0      12.0       0.0                              0.0
0.6        -0.396
  9 1.0     17 2.0
143
MnF+         200 1.0       2.0       0.0                              0.0
 0.84       0.0
  9 1.0     20 1.0
144
Mn+3         200 3.0       3.0       0.0                              0.0
 -25.51     25.8
  9 1.0      2 -1.0
150
AlOH+2       310 2.0       0.0       0.0                              0.0
-5.00      11.49     -38.253     0.0        -656.27     14.327
 10 1.0      3 1.0     1 -1.0
151
AlOH2+       310 1.0       0.0       0.0                              0.0
-10.1      26.90     88.500      0.0        -9391.6     -27.121
 10 1.0      3 2.0     1 -2.0
```

```
152
AlOH3       310 0.0       0.0       0.0                           1.0
-16.9     39.89      226.374     0.0         -18247.8    -73.597
 10 1.0     3 3.0     1 -3.0
153
AlOH4-      310 -1.0      0.0       0.0                           2.0
-22.7     42.30      51.578      0.0         -11168.9    -14.865
 10 1.0     3 4.0     1 -4.0
154
AlSO4+      200 1.0       6.0       0.0                           0.0
 3.02      2.15
 10 1.0    16 1.0
155
AlSO42-     200 -1.0      12.0      0.0                           0.0
 4.92      2.84
 10 1.0    16 2.0
156
AlHSO4+2    200 2.0       +6.0
2.448
 10 1.0    16  1.0    1  1.0
157
AlF+2       200 2.0       0.0       0.0                           0.0
 7.0       1.06
 10 1.0    20 1.0
158
AlF2+       200 1.0       0.0       0.0                           0.0
 12.7      1.98
 10 1.0    20 2.0
159
AlF3        200 0.0       0.0       0.0                           0.0
 16.8      2.16
 10 1.0    20 3.0
160
AlF4-       200 -1.0      0.0       0.0                           0.0
 19.4      2.20
 10 1.0    20 4.0
161
AlF5-2      200 -2.0      0.0       0.0                           0.0
 20.6      1.84
 10 1.0    20 5.0
162
AlF6-3      200 -3.0      0.0       0.0                           0.0
 20.6     -1.67
 10 1.0    20 6.0
164
H3SiO4-     210 -1.0      0.0       0.0                           1.0
 -9.83     6.12      -302.3724   -0.050698   15669.69    108.18466   -1119669.0
 13 1.0     1 -1.0
165
H2SiO4-2    210 -2.0      0.0       0.0                           2.0
 -23.0     17.6      -294.0184   -0.072650   11204.49    108.18466   -1119669.0
 13 1.0     1 -2.0
166
SiF6-2      400 -2.0      0.0       0.0                           0.0
 30.18    -16.26
 13 1.0     1 4.0     20 6.0    3 -4.0
170
BaOH+       300 1.0       0.0       0.0                           1.0
 -13.47
```

```
 11 1.0     3 1.0     1 -1.0
171
BaCO3       210 0.0     4.0       0.0                           0.0
2.71       3.55      0.113       0.008721
 11 1.0    15 1.0
172
BaHCO3+     310 1.0     4.0       0.0                           0.0
 11.311    1.999     104.7933    0.04619749  -5151.79    -38.92561   563713.9
 11 1.0    15 1.0     1 1.0
173
BaSO4       200 0.0     6.0       0.0                           0.0
2.7
 11 1.0    16 1.0
176
SrOH+       301 1.0     0.0       5.0       5.0                 1.0
 -13.29
 12 1.0     3 1.0     1 -1.0
177
SrHCO3+     311 1.0     4.0       5.4       5.4                 1.0
 11.509    2.489    104.6391    0.04739549  -5151.79    -38.92561   563713.9
 12    1.0 15    1.0 1    1.0
178
SrCO3       210 0.0     4.0                                     2.0
 2.81      5.22     -1.019      0.012826
 12    1.0 15    1.0
179
SrSO4       200 0.0     6.0
 2.29      2.08
 12    1.0 16    1.0
180
LiOH        300 0.0     0.0       0.0                           1.0
 -13.64   0.0
 21 1.0     3 1.0     1 -1.0
181
LiSO4-      200 -1.0    6.0       0.0                           0.0
0.64      0.0
 21 1.0    16 1.0

LOOK MIN
Calcite    2   4.0       -8.480    -2.297         1
  15 1.0          4 1.0
-171.9065   -.077993    2839.319      71.595
Aragonit   2   4.0       -8.336    -2.589         1
  15 1.0          4 1.0
-171.9773   -.077993    2903.293      71.595
Dolomite   3   8.0       -17.09    -9.436         0
   4 1.0          5 1.0         15 2.0
Siderite   2   6.0       -10.89    -2.48          0
   8 1.0         15 1.0
Rhodochr   2   6.0       -11.13    -1.43          0
   9 1.0         15 1.0
Strontit   2          4.0    -9.271    -0.40      1
  12        1.0  15        1.0
155.0305               -7239.594   -56.58638
Witherit   2          4.0    -8.562    0.703      1
  11        1.0  15        1.0
607.642    0.121098    -20011.25   -236.4948
Gypsum     3   6.0       -4.58     -0.109         1
```

```
   4 1.0         16 1.0          3 2.0
68.2401                 -3221.51    -25.0627
Anhydrite  2   6.0       -4.36     -1.71          1
   4 1.0         16 1.0
197.52                  -8669.8     -69.835
Celestit   2   6.0       -6.63     -1.037         1
  12 1.0         16 1.0
-14805.9622  -2.4660924  756968.533  5436.3588   -40553604.0
Barite     2   6.0       -9.97     6.35           1
  11 1.0         16 1.0
 136.035      0.0        -7680.41    -48.595
Hydroxap   4   0.0       -3.421    -36.155        0
   3 1.0         65 3.0          4 5.0          1 -4.0
Fluorite   2   0.0       -10.6     4.69           1
   4 1.0         20 2.0
66.348                  -4298.2     -25.271
SiO2 (a)   2   0.0       -2.71     3.34           1
  13 1.0          3 -2.0
 -0.26       0.0         -731.0
Chalcedy   2   0.0       -3.55     4.72           1
  13 1.0          3 -2.0
 -0.09       0.0         -1032.0
Quartz     2   0.0       -3.98     5.99           1
  13 1.0          3 -2.0
 0.41        0.0         -1309.0
Gibbs(c)   3          0.0     8.11    -22.8        0
  10        1.0   3        3.0   1       -3.0
Al(OH)3a   3          0.0    10.8     -26.5        0
  10        1.0   3        3.0   1       -3.0
Kaolinit   4          0.0     7.435    -35.3       0
   3        1.0   1       -6.0  13        2.0  10        2.0
Albite     4          0.0    -18.000    25.896       0
   6        1.0 153        1.0  13        3.0   3       -8.0
Anorth     4          0.0    -19.330    17.530       0
   4        1.0 153        2.0  13        2.0   3       -8.0
Microcln   5          0.0     0.875   -12.467       0
  10        1.0  13        3.0   7        1.0   3       -4.0   1       -4.0
Muscovit   4          0.0     12.97   -59.377       0
  10        3.0  13        3.0   7        1.0   1      -10.0
Chlorite   5          0.0    -90.610    54.760       0
   3      -10.0   5        5.0 153        2.0  13        3.0  31        8.0
Ca-Mont    5          0.0    -45.000    58.373       0
   3      -12.0   4      0.165 153       2.33  13       3.67   1        2.0
Talc       4          0.0    -62.290    45.065       0
   3      -10.0   5        3.0  13        4.0  31        6.0
Illite     6          0.0    -40.310    54.684       0
   3      -11.2   7        0.6   5       0.25 153        2.3  13        3.5
   1        1.2
Chrysotl   4          0.0     32.2     -46.8       1
   3        1.0   1       -6.0  13        2.0   5        3.0
13.248       0.0         10217.1     -6.1894     0.0
Sepiolit   4   0.0       15.76     -10.7          0
   5 2.0        13 3.0          1 -4.0         3  -0.5
Hematite   3   3.0       -4.008    -30.845        0
```

```
 115 2.0          3 3.0          1 -6.0
Goethite   3   3.0       -1.0                      0
 115 1.0          3 2.0          1 -3.0
Fe(OH)3a   3   3.0       4.891     0.0             0
 115 1.0          3 3.0          1 -3.0
Pyrite     4     0.0     -18.48     11.3           0
   1  -2.0        2  -2.0        8  1.0        42  2.0
FeS ppt    3   0.0       -3.915    0.0             0
   8 1.0         42 1.0          1 -1.0
Vivianit   3   6.0       -36.000   0.0             0
   8 3.0         19 2.0          3 8.0
Pyrolusi   4   4.0       41.38     -65.11          0
   9 1.0          3 2.0          1 -4.0         2 -2.0
Hausmani   4   8.0       61.03     -100.64         0
   9 3.0          3 4.0          1 -8.0         2 -2.0
Manganit   4   3.0       25.34                     0
   9 1.0          3 2.0          1 -3.0         2 -1.0
Pyrochro   3   2.0       15.2                      0
   9 1.0          3 2.0          1 -2.0
PCO2       1     4.0      -1.468    -4.776         1
  35  1.0
108.3865   0.01985076  -6919.53    -40.45154    669365.0
O2 gas     1     4.0      -2.96      -1.844        0
  32  1.0
H2 gas     1     -2.0     -3.15      -1.759        0
  33  1.0
Melanter   3     8.0     -2.209     4.91           1
   3 7.0          8 1.0         16 1.0
 1.447       -0.004153   0.0         0.0         -214949.0
Alunite    5     12.0    -1.4      -50.25          0
  10 3.0          3 6.0          1 -6.0         7 1.0         16 2.0
K-Jarosit  5     21.0    -9.21     -31.28          0
 115 3.0          3 6.0          1 -6.0         7 1.0         16 2.0

END
```

Attachment B. - Program listing of PHREEQE

```
C
C          *********************************************
C
C                         PROGRAM PHREEQE
C
C          D.L. PARKHURST, D.C. THORSTENSON, L.N. PLUMMER
C
C                VERSION CURRENT - AUGUST 1, 1990
C
C          *********************************************
C
C
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C
C         Three files are required by the program:  (1) input file,
C         (2) output file, and (3) data base.  The FORTRAN unit
C         numbers for these files are set at compile time by a
C         PARAMETER statement in the COMMON.BLOCKS file.
C         The parameters names and default settings are:
C         IR = 5, input file; IW = 6, output file; and IDB = 11,
C         data base.
C
C         The three files are NOT opened within the FORTRAN code.
C         Either (1) the files can be opened externally to the program
C         or (2) the FORTRAN code can be modified to include OPEN
C         statements.
C
      DMAX=10.0
      DMIN=0.7
      FUDGE=1D0
      RMAX=20.0
      RMIN=0.9D0
      CNVG1=0.1
      CNVG2=1.0D4
      ITMAX=200
      CHKMU=1D3
      DO 10 I=1,MAXS
      NSP(I)=0
   10 CONTINUE
      CALL RDATA
      CLOSE (UNIT=IDB)
   20 CONTINUE
C          SINGLE SIMULATION LOOP
      CALL READ
      ISTEP=0
C          SOLVE INITIAL SOLUTIONS
      DO 40 ISOL=1,2
      IF (ISOLV(ISOL).EQ.0) GO TO 40
      CALL SOLN
      IESPEC=IOPT(2)
      IF (IOPT(2).GE.2) IESPEC=0
      CALL PICK1
      CALL PTOT
      CALL KTEMP
      CALL MODEL
      IF (IOPT(2).LT.2) GO TO 30
      IESPEC=LNEG
      IF (ELECT.LT.0D0) IESPEC=LPOS
      CALL PICK1
      CALL KTEMP
```

```
      CALL MODEL
      TOTAL(ISOL,IESPEC)=TOT(IESPEC)
   30 CONTINUE
      IF (IASPEC.GT.0) TOTAL(ISOL,IASPEC)=TOT(IASPEC)
      CALL THORIT(T)
      TH(ISOL)=T
      THOR=T
      DIFFZ(ISOL)=ELECT
      CALL PSPEC
      CALL PLOOK
   40 CONTINUE
      IF (IOPT(3).EQ.0) GO TO 20
C          TAKE REACTION STEPS
      DO 50 ISTEP=1,MAX0(1,NSTEPS)
      CALL STEP
      CALL PTOT
      CALL PICK2
      CALL KTEMP
      CALL KMIN
      CALL MODEL
      CALL PPHASE
      CALL PLOOK
      CALL PTOT
      CALL PSPEC
   50 CONTINUE
      CALL SAVE
      GO TO 20
      END
      SUBROUTINE MODEL
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      CALL ZEROAR
      CALL SET
      ITER=0
      JTER=0
   10 CONTINUE
      ITER=ITER+1
      CALL GAMMA
      CALL ZEROAR
      CALL AQMOD
      CALL CHECK(*30,*40,*10)
      CALL SOLVE
      CALL RESET
      GO TO 10
   40 CONTINUE
      JTER=JTER+1
      CALL SOLVE2
      GO TO 10
   30 CONTINUE
      RETURN
      END
      SUBROUTINE SET
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      LA(1)=DLOG10(TOT(1))
      LA(2)=DLOG10(TOT(2))
      LA(3)=0.0D0
      PH=-LA(1)
      PE=-LA(2)
      M(1)=1D1**(LA(1))
      DO 10 I=4,LASTT
      IF (IIN(I).LE.0) GO TO 10
```

```
      IF (TOT(I).LE.0.0D0) TOT(I)=1D-10
      M(I)=0.1D0*TOT(I)
      LA(I)=DLOG10(M(I))
   10 CONTINUE
      DO 20 I=MAXT1,LASTS
      M(I)=0.0D0
   20 CONTINUE
      OLDC=CNVG1
      CNVG1=1D3
      ITER=0
      JTER=0
      CALL GAMMA
   30 CONTINUE
      JTER=JTER+1
      IF(JTER.LT.5) GO TO 35
      IF(IOPT(8).GT.0) WRITE(IW,45)
   45 FORMAT(1X,80('*')/1X,'DID NOT CONVERGE IN SET.')
      GO TO 50
   35 CONTINUE
      CALL AQMOD
      CALL SOLVE2
      CALL CHECK(*50,*60,*60)
   60 CONTINUE
      CALL ZEROAR
      IF(JCHECK.EQ.0) GO TO 50
      GO TO 30
   50 CONTINUE
      CNVG1=OLDC
      RETURN
      END
      SUBROUTINE GAMMA
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      DOUBLE PRECISION MUHALF
      SAVE DSUM,OLDMU
C          CALCULATE IONIC STRENGTH
      OLDMU=MU
      SUM=M(1)
      MU=M(1)
      DO 10 I=4,LASTS
      IF (SFLAG(I).EQ.0) GO TO 10
      SUM=SUM+M(I)
      MU=MU+M(I)*ZSP(I)*ZSP(I)
   10 CONTINUE
      IF (ITER.LE.1) GO TO 20
      IF (SUM-DSUM.LT.1D0) GO TO 20
      SUM=DSUM+1D0
   20 CONTINUE
      DSUM=SUM
      MU=MU*0.5D0
      IF(ITER.LE.1) GO TO 30
C
C                  SLOW DOWN CHANGES IN MU AT HIGH IONIC STRENGTH
C
      FACTOR=1.0D0
      IF(MU.GT.1D0) FACTOR=0.3D0
      FUDGE=1.0D0
      IF(MU.GT.1D0) FUDGE=0.3D0
      MU=OLDMU+(MU-OLDMU)*FACTOR
   30 CONTINUE
      IF(MU.GT.1D2) MU=1D2
```

```
      MUHALF=DSQRT(MU)
C          ACTIVITY OF WATER
      AH2O=1.0-SUM*0.017
      IF (SUM.GT.40.0D0) AH2O=0.32
      LA(3)=DLOG10(AH2O)
      TOT(3)=AH2O
C          CALCULATE ACTIVITY COEFFICIENTS
      AMU=-A*MUHALF
      BMU=B*MUHALF
      CMU=-A*(MUHALF/(1.0+MUHALF)-0.3*MU)
      ZCHRG=0.1*MU
      LG(1)=AMU/(1.0+DHA(1)*BMU)
      IF (IOPT(6).EQ.1) LG(1)=CMU
      LG(2)=0.0D0
      LG(3)=0.0D0
      DO 70 I=4,LASTS
      IF (SFLAG(I).EQ.0) GO TO 70
      IF (DABS(ZSP(I)).LT.1.0D-40) GO TO 40
      IF (GFLAG(I).EQ.1) GO TO 50
      IF (DHA(I).LE.0D0) GOTO 60
      IF (IOPT(6).EQ.1) GO TO 60
C                  EXTENDED DEBYE-HUCKEL WITH ION SIZE PARAMETER
      LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+DHA(I)*BMU)
      GO TO 65
C                  GAMMA FOR UNCHARGED SPECIES
   40 LG(I)=ZCHRG
      GO TO 65
C                  WATEQ DEBYE-HUCKEL
   50 LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+ADHSP(I,1)*BMU)+ADHSP(I,2)*MU
      GO TO 65
C                  DAVIES GAMMA
   60 LG(I)=CMU*ZSP(I)*ZSP(I)
   65 CONTINUE
      IF(LG(I).LT.-1D1) LG(I)=-1D1
      IF(LG(I).GT.1D1) LG(I)=1D1
   70 CONTINUE
      RETURN
      END
      FUNCTION PTZGAM(Z,B0,B1,C,MU)
C
C                  FUNCTION USES PIZTER PARAMETERS TO CALCULATE FREE ION
C                  ACTIVITY COEFFICIENTS BY THE METHOD OF MILLERO AND THE
C                  MCGINNIS ASSUMPTION.
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION MU,MUHALF,LGAMMA
      MUHALF=DSQRT(MU)
      F1=1.0-DEXP(-2.0*MUHALF)*(1+2.0*MUHALF-2.0*MU)
      FG=-0.392*(MUHALF/(1.0+1.2*MUHALF)+2.0/1.2*DLOG(1.0+1.2*MUHALF))
      LGAMMA=Z*Z*FG + MU*B0 + F1*B1 + MU*MU*C
      PTZGAM=LGAMMA/2.303D0
      RETURN
      END
      SUBROUTINE AQMOD
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      ELECT=0D0
      THSOLN=0D0
      DALKS=0D0
C
C                  CALCULATE JACOBIAN
```

```
C
      ZSP(2)=0D0
      DO 20 I=1,LASTS
      IF(SFLAG(I).EQ.0) GO TO 20
      DM=LKSP(I)-LG(I)
      DO 60 J=1,NSP(I)
      DM=DM+LA(LSP(I,J))*CSP(I,J)
   60 CONTINUE
      LM(I)=DM
      M(I)= UNDER(LM(I))
      IF(M(I).GT.1D1.AND.I.NE.2.AND.IOPT(8).GT.0)
     1     WRITE(IW,80) I,SNAME(I),M(I)
   80 FORMAT(1X,I3,2X,A10,2X,1PD10.2,' = MOLALITY')
C
C                    SUM MOLALITIES INTO PROPER ROWS AND COLUMNS
C
      DO 100 I1=1,NSP(I)
      DM=M(I)*CSP(I,I1)
      K2=LSP(I,I1)
      IF(K2.GE.4) CALCT(K2)=CALCT(K2)+DM
C
C                    MASS BALANCES
C
      DO 120 J1=1,NSP(I)
      K1=LSP(I,J1)
      IF(K1.LT.4) GO TO 120
      AR(K1,K2)=AR(K1,K2)+DM*CSP(I,J1)
  120 CONTINUE
C                    ELECTRICAL BALANCE
      AR(1,K2)=AR(1,K2)+DM*ZSP(I)
C                    THOR BALANCE
      AR(2,K2)=AR(2,K2)+DM*THSP(I)
C                    ALKALINITY EQUATION
      AR(3,K2)=AR(3,K2)+DM*ALKSP(I)
  100 CONTINUE
C                    SUM TOTAL ELECT, THOR, ALK
      THSOLN=THSOLN+M(I)*THSP(I)
      ELECT=ELECT+M(I)*ZSP(I)
      DALKS=DALKS+M(I)*ALKSP(I)
   20 CONTINUE
      ZSP(2)=-1D0
C     *****
      ENTRY SI
C     *****
      IF (NMINS.EQ.0) RETURN
      DO 140 I=1,NMINS
      J=MAXT+I
      K=NMIN(I)
C                    CALCULATE INVERSE SATURATION INDEX
      DSI=LKMIN(I)
      DO 130 I1=1,K
      DSI=DSI-LA(LMIN(I,I1))*CMIN(I,I1)
  130 CONTINUE
      CR(J)=DSI*DLOG(1D1)
  140 CONTINUE
      RETURN
      END
      SUBROUTINE CHECK(*,*,*)
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      DOUBLE PRECISION MCLOSE
```

```
      SAVE OLDMU, OLDH2O
      DATA ECLOSE,TCLOSE,THCLOS,MCLOSE /1D-10,1D-7,1D-7,1D-5/
      ICHECK=0
      LCHECK=0
      JCHECK=0
      MCHECK=0
      IF(ITER.LE.1) GO TO 20
C
C                   CHECK CHANGE IN AH20 AND MU
C
      MCHECK=0
      IF(DABS(MU-OLDMU).GT.CHKMU) MCHECK=1
   20 CONTINUE
      OLDH2O=TOT(3)
      OLDMU=MU
C
C                   CALCULATE FUNCTION RESIDUALS
C
      CR(1)=DZOFF-ELECT
      CR(2)=THOR-THSOLN
      CR(3)=DALKT-DALKS
      DO 30 I=4,LASTT
      IF(IIN(I).LE.0) GO TO 30
      CR(I)=TOT(I)-CALCT(I)
   30 CONTINUE
C                   CHECK FOR CONVERGENCE
C
C                   ELECTRICAL BALANCE
      DCHECK=MU*ECLOSE
      IF(IESPEC.GT.0.AND.DABS(CR(1)).GT.DCHECK) ICHECK=1
C                   THOR
      IF(IIN(2).GT.0.AND.DABS(CR(2)).GT.MU*THCLOS) ICHECK=1
C                   ALKALINITY
      IF(IASPEC.GT.0.AND.DABS(CR(3)).GT.TCLOSE*DALKT) ICHECK=1
C                   MINERALS
      IF(NMINS.EQ.0) GO TO 40
      DO 60 I=1,NMINS
      K=MAXT+I
      IF(DABS(CR(K)).GT.MCLOSE) ICHECK=1
   60 CONTINUE
   40 CONTINUE
C                   MASS BALANCES
      DO 80 I=4,LASTT
      IF(IIN(I).LE.0) GO TO 80
      IF(I.EQ.IESPEC.OR.I.EQ.IASPEC) GO TO 80
      IF(DABS(CR(I)).GT.TCLOSE*TOT(I)) ICHECK=1
      DT=DABS(1D0-CALCT(I)/TOT(I))
      IF(DT.GT.CNVG1) JCHECK=1
      IF(DT.GT.CNVG2) LCHECK=1
   80 CONTINUE
C
C                   RETURNS
C
      IF(ITER.GT.ITMAX) GO TO 100
      IF(ITER.LT.5) ICHECK=1
C                                                   /* MU CHANGE TOO LARGE
      IF(MCHECK.EQ.1) RETURN 3
C                                                   /* VERY POOR MASS BALANCE
      IF(LCHECK.EQ.1) RETURN 2
C                                                   /* POOR MASS BALANCE
```

```
      IF(JCHECK.EQ.1) RETURN
C                                                  /* CONVERGED
      IF(ICHECK.EQ.0) RETURN 1
C                                                  /* NEW ITER WITH ALL EQNS.
      RETURN
  100 CONTINUE
      DT=99.0
      WRITE(IW,120) ITER
  120 FORMAT(1H1,80('*')//'CALCULATIONS TERMINATED AT ',
     1     I5,' ITERATIONS.')
      CALL PBUG(DT,DT)
      CALL PTOT
      CALL PSPEC
      CALL PPHASE
      CALL PLOOK
      ENDFILE (UNIT=IW)
      STOP
      END
      SUBROUTINE SOLVE
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C                    COPY ROWS OF JACOBIAN AR INTO ARRAY AS
C                    WHICH IS SOLVED BY SLNQ
C
C                    PUT ELECTRICAL BALANCE EQUATION IN ROW IESPEC
      IF (NEQ.EQ.0) RETURN
      IF (IESPEC.LT.2) GO TO 20
      TOT(IESPEC)=CALCT(IESPEC)
      CR(IESPEC)=-ELECT
      DO 40 I=1,LASTT
      AR(IESPEC,I)=AR(1,I)
   40 CONTINUE
   20 CONTINUE
C            PUT ALKALINITY EQUATION IN PLACE OF MASS BALANCE
      IF (IASPEC.EQ.0) GO TO 60
      TOT(IASPEC)=CALCT(IASPEC)
      CR(IASPEC)=CR(3)
      DO 80 I=1,LASTT
      AR(IASPEC,I)=AR(3,I)
   80 CONTINUE
   60 CONTINUE
C                    DECIDE WHICH EQUATIONS ARE INCLUDED
C
C                    GENERATE INDICES TO COPY INTO ARRAY AS (IRS)
C                    AND TRANSFER DELTAS BACK TO ARRAY AR NUMBERING (ISR)
C
C                    INCLUDE ONLY MASS BALANCE EQUATIONS
      IF(JCHECK.EQ.0) GO TO 100
      ICOUNT=0
      DO 120 I=1,3
      IRS(I)=0
  120 CONTINUE
      DO 140 I=4,MAXT
      IRS(I)=0
      IF(IIN(I).EQ.0) GO TO 140
      ICOUNT=ICOUNT+1
      IRS(I)=ICOUNT
      ISR(ICOUNT)=I
  140 CONTINUE
      NFT=1
      NLT=ICOUNT
```

```
      IMINS=0
      NSR=ICOUNT
      NRS=LASTT
      GO TO 200
  100 CONTINUE
C                    INCLUDE ALL EQUATIONS
      DO 220 I=1,MAXT
      IRS(I)=IIN(I)
      IF(IIN(I).GT.0) THEN
         ISR(IIN(I))=I
      END IF
  220 CONTINUE
      NFT=IFT
      NLT=ILT
      IMINS=NMINS
      IF(NMINS.EQ.0) GO TO 240
      DO 260 I=1,NMINS
      J=MAXT+I
      K=ILT+I
      IRS(J)=K
      ISR(K)=J
  260 CONTINUE
  240 CONTINUE
      NRS=MAXT+NMINS
      NSR=NEQ
  200 CONTINUE
C
C                    COPY TO ARRAY AS
C
      NSR1=NSR+1
      DO 300 I=1,NRS
      IF(IRS(I).EQ.0) GO TO 300
      K1=IRS(I)
      DO 310 J=1,NRS
      IF(IRS(J).EQ.0) GO TO 310
      K2=IRS(J)
      AS(K1,K2)=AR(I,J)
  310 CONTINUE
      AS(K1,NSR1)=CR(I)
  300 CONTINUE
C
C                    SOLVE FOR DA/A
C
      CALL SLNQ (NSR,AS,AS,DELTA,IOPT9,MAXEQ,IW)
      RETURN
      END
      SUBROUTINE SOLVE2
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      IF(IOPT(8).GT.0) WRITE(IW,80) ITER,JTER
   80 FORMAT(1X,'SOLVE2.  ITER =',I4,'    JTER =',I4)
      DO 40 I=4,LASTT
      IF(IIN(I).LE.0) GO TO 40
      IF(CALCT(I).LE.0D0) CALCT(I)=1D-30
      TLA=LA(I)+(DLOG10(TOT(I))-DLOG10(CALCT(I)))
      IF(IOPT(8).GT.0) WRITE(IW,60) SNAME(I),LA(I),TLA,CALCT(I)
   60 FORMAT(1X,A12,2F12.3,1PD12.2)
      LA(I)=TLA
   40 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SLNQ (N,AS,AS1,DELTA,IOPT9,MAXEQ,IW)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z),INTEGER(I-N)
      DIMENSION AS(MAXEQ,MAXEQ),DELTA(MAXEQ),AS1(MAXEQ*MAXEQ)
C
C     SOLUTION OF N LINEAR EQUATIONS IN N UNKNOWNS BY GAUSSIAN
C     ELIMINATION.
C
C     N      INDICATES THE ORDER OF THE MATRIX,
C     AS     CONTAINS THE MATRIX OF THE COEFFICIENTS,
C     AS1    IS A ONE-DIMENSIONAL ARRAY EQUIVALENCED TO AS,
C     DELTA  CONTAINS THE N VALUES OF THE UNKNOWNS,
C     IOPT9  EQUAL TO 1, PRINTS AS AND DELTA,
C     MAXEQ  IS THE LEADING DIMENSION OF AS.
C
C                                         initialize
      IF (N.EQ.0) RETURN
      NP1=N+1
      NM1=N-1
C                                         print array if iopt(9)=1
      IF (IOPT9.EQ.1) THEN
         DO 10 II=1,N
         WRITE(IW,240) (AS(II,JJ),JJ=1,NP1)
   10    CONTINUE
      END IF
C                                         trivial case
      IF (N.EQ.1) THEN
         IF (DABS(AS(1,1)).LT.1.0D-40) GO TO 160
         DELTA(1)=AS(1,2)/AS(1,1)
         GO TO 180
      END IF
C                                         reduction loop
      DO 120 I=1,NM1
      K=I+1
      M=I
      B=DABS(AS(I,I))
      LL=MAXEQ*(I-1)
C                                         find largest element in column
      DO 40 L=LL+K,LL+N
      BB=DABS(AS1(L))
      IF (B.LT.BB) THEN
         M=L-LL
         B=BB
      END IF
   40 CONTINUE
      IF (B.EQ.0D0) GO TO 160
C                                         exchange rows if necessary
      IF (I.NE.M) THEN
         DO 70 L=I,NP1
         B=AS(I,L)
         AS(I,L)=AS(M,L)
   70    AS(M,L)=B
      END IF
C                                         reduction step
      CC=1D0/AS1(LL+I)
      DO 115 M=K,N
      B=-AS1(LL+M)
      IF (B.EQ.0D0) GO TO 115
      B=B*CC
      DO 110 L=K,NP1
  110 AS(M,L)=AS(M,L)+B*AS(I,L)
```

```
  115 CONTINUE
  120 CONTINUE
C                                   calculation of delta(n)
      IF(DABS(AS(N,N)).GT.1.0D-40) THEN
         DELTA(N)=AS(N,NP1)/AS(N,N)
      ELSE
         WRITE(IW,320) N
  320    FORMAT(1X,'AS(N,N)=0D0.  N=',I3)
         DELTA(N)=0D0
      END IF
C                                   back substitution for other rows
      LL=MAXEQ*N
      DO 400 K=NM1,1,-1
      B=-AS1(LL+K)
      DO 410 L=K+1,N
  410 B=B+AS(K,L)*DELTA(L)
      DELTA(K)=-B/AS(K,K)
  400 CONTINUE
C                                   print results if iopt9.eq.1
  180 CONTINUE
      IF (IOPT9.EQ.1) THEN
         WRITE(IW,220)
         WRITE(IW,230) (DELTA(I),I=1,N)
         WRITE(IW,250)
      END IF
      RETURN
C                                   singular matrix
  160 WRITE(IW,260)
      ENDFILE (UNIT=IW)
      STOP
C
C
  220 FORMAT (1X,'DELTA VALUES')
  230 FORMAT (3X,1P6D12.3)
  240 FORMAT (/(3X,1P6D12.3))
  250 FORMAT (1X)
  260 FORMAT (1H1,'THE PHASE RULE HAS BEEN VIOLATED')
      END
      SUBROUTINE STEP
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      IF (IOPT(3).EQ.0) GO TO 120
      I=IOPT(3)
      WRITE(IW,140) ISTEP
      GO TO (10,30,50,60,100,100), I
      GO TO 100
C          MIX SOLUTION 1 WITH SOLUTION 2
   10 CONTINUE
      X1=XSTEP(ISTEP)
      X2=1.0-X1
      IF(X1.LT.0.0) X1=0.0
      IF(X2.LT.0.0) X2=0.0
      DO 20 I=1,MAXT
      TOT(I)=X1*TOTAL(1,I)+X2*TOTAL(2,I)
   20 CONTINUE
      THOR=TH(1)*X1+TH(2)*X2
      TC=X1*TEMP(1)+X2*TEMP(2)
      IF(X1.GT.1.0) TC=TEMP(1)
      IF(X2.GT.1.0) TC=TEMP(2)
      DZOFF=X1*DIFFZ(1)+X2*DIFFZ(2)
      WRITE(IW,150) X1,X2
```

```
      GO TO 120
C          TITRATE
   30 CONTINUE
      X1=XSTEP(ISTEP)
      VTOT=V0+X1
      TOT(1)=1D1**((DLOG10(TOTAL(1,1))*V0+DLOG10(TOTAL(2,1))*X1)/VTOT )
      TOT(2)=1D1**((DLOG10(TOTAL(1,2))*V0+DLOG10(TOTAL(2,2))*X1)/VTOT )
      DO 40 I=3,MAXT
      TOT(I)=(TOTAL(1,I)*V0+TOTAL(2,I)*X1)/VTOT
   40 CONTINUE
      TC=(TEMP(1)*V0+TEMP(2)*X1)/VTOT
      THOR=(TH(1)*V0+TH(2)*X1)/VTOT
      DZOFF=(DIFFZ(1)*V0+DIFFZ(2)*X1)/VTOT
      WRITE(IW,160) X1
      GO TO 120
C          ADD REACTION IN INCREMENTS
   50 CONTINUE
      X1=XSTEP(ISTEP)
      GO TO 70
C            ADD REACTION LINEARLY
   60 CONTINUE
      X1=(ISTEP*XSTEP(1))/NSTEPS
   70 CONTINUE
      DZOFF=DIFFZ(1)
      DO 80 I=1,MAXT
      TOT(I)=TOTAL(1,I)
   80 CONTINUE
      DO 90 I=1,NCOMPS
      K=LREAC(I)
      IF (K.EQ.0) DZOFF=DIFFZ(1)+X1*CREAC(I)
      IF (K.LT.4.OR.K.GT.MAXT) GO TO 90
      TOT(K)=TOT(K)+X1*CREAC(I)
   90 CONTINUE
      THOR=TH(1)+THREAC*X1
      TC=TEMP(1)
      IF (ISTEP.GT.1) TOT(1)=1D1**LA(1)
      WRITE(IW,170) X1
      CALL PREAC
      GO TO 120
C          FOLLOW PHASE BOUNDARIES ONLY
  100 CONTINUE
      DO 110 I=1,MAXT
      TOT(I)=TOTAL(1,I)
  110 CONTINUE
      THOR=TH(1)
      TC=TEMP(1)
      DZOFF=DIFFZ(1)
      WRITE(IW,180)
  120 CONTINUE
C          TEMPERATURE
      IF (IOPT(4).EQ.0) GO TO 130
      IF (IOPT(4).EQ.1) TC=TSTEP(1)
      IF (IOPT(4).EQ.2) TC=(ISTEP*(TSTEP(2)-TSTEP(1)))/NSTEPS+TSTEP(1)
      IF (IOPT(4).EQ.3) TC=TSTEP(ISTEP)
      WRITE(IW,190) TC
  130 CONTINUE
      TK=TC+273.15
      RETURN
C
  140 FORMAT (1H1,'STEP NUMBER',I3,/1H0,14('-'))
```

```
  150 FORMAT (1H0,F10.3,' = FRACTION OF SOLUTION 1.',3X,F10.3,' = FR',
     1'ACTION OF SOLUTION 2.'//)
  160 FORMAT (1H0,F10.3,' VOLUME UNITS OF SOLUTION 2 HAVE BEEN ',
     1'ADDED.'//)
  170 FORMAT (1H0,1PD10.3,' MOLES OF REACTION HAVE BEEN ADDED.'//)
  180 FORMAT (//)
  190 FORMAT (23X,F10.2,' = NEW TEMPERATURE (C).'//)
      END
      FUNCTION UNDER(D)
      DOUBLE PRECISION D,UNDER
      UNDER=0D0
      IF (D.LT.-33.0D0) GO TO 10
      UNDER=1D5
      IF (D.GT.5D0) GO TO 10
      UNDER=1D1**D
   10 CONTINUE
      RETURN
      END
      SUBROUTINE RESET
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C
C                    CALCULATE CHANGE IN TOTALS DUE TO
C                    MINERAL SOLUTION/PRECIPITATION
C
      F=1D0
      FPHPE=1D0
      IF(IMINS.EQ.0) GO TO 40
      DO 60 I=IFT,ILT
      DT=0D0
      DO 80 J=IFM,ILM
      K=MAXT+(J-ILT)
      DT=DT-DELTA(J)*AR(ISR(I),K)
   80 CONTINUE
      DELTOT(I)=DT
C
C                    MAKE SURE NO NEGATIVE TOTALS OCCUR
C
      IF(TOT(IOUT(I))+DT.GT.0D0) GO TO 60
      DF=-RMIN*TOT(IOUT(I))/DT
      IF(DF.LT.F) F=DF
   60 CONTINUE
C
C                    MAKE SURE NO LARGE CHANGES IN MINERALS
C
      DO 70 I=IFM,ILM
      IF(DABS(DELTA(I)).LT.1D0) GO TO 70
      DF=DABS(1D0/DELTA(I))
      IF (DF.LT.F) F=DF
   70 CONTINUE
   40 CONTINUE
C
C                    ENSURE PH CHANGE IS SMALL
      DF=1D0
      IF(IRS(1).EQ.0) GO TO 120
      IF(DELTA(1).LT.-DMIN) DF=-DMIN/DELTA(1)
      IF(DELTA(1).GT.DMAX)  DF=DMAX/DELTA(1)
      FPHPE=DF
  120 CONTINUE
C
C                    ENSURE PE CHANGE IS SMALL
```

```
C
      IF(IRS(2).EQ.0) GO TO 140
      IF(DELTA(IRS(2)).LT.-DMIN) DF=-DMIN/DELTA(IRS(2))
      IF(DELTA(IRS(2)).GT.DMAX)  DF=DMAX/DELTA(IRS(2))
      IF(DF.LT.FPHPE) FPHPE=DF
  140 CONTINUE
C
C                   SCALE DELTAS
C
      IF(IRS(1).GT.0) DELTA(1)=DELTA(1)*FPHPE
      IF(IRS(2).GT.0) DELTA(2)=DELTA(2)*FPHPE
C     IF(FPHPE.LT.1D-5.AND.DELTA(1).LT.1D-4)
C    1      DELTA(1=DELTA(1)*DABS(DELTA(2)/(DELTA(1)*1D1)
C
C                   MAKE SURE NO NEGATIVE ACTIVITIES ARE CALCULATED
C
      DF=1D0
      DO 160 I=NFT,NLT
      IF(DELTA(I).LT.-RMIN) DF=-RMIN/DELTA(I)
      IF(DELTA(I).GT.RMAX) DF=RMAX/DELTA(I)
      IF(DF.LT.F) F=DF
  160 CONTINUE
C
C                   SCALE DELTAS
C
      DO 180 I=NFT,NSR
      DELTA(I)=DELTA(I)*F
  180 CONTINUE
      IF(IMINS.EQ.0) GO TO 200
      DO 220 I=NFT,NLT
      DELTOT(I)=DELTOT(I)*F
  220 CONTINUE
  200 CONTINUE
C
      IF(IOPT(8).EQ.1) CALL PBUG(F,FPHPE)
C
C                   RESET ACTIVITIES
C
      DO 300 I=1,NLT
      K=ISR(I)
      LA(K)=LA(K)+DLOG10(1D0+FUDGE*DELTA(I))
  300 CONTINUE
      TOT(1)=1D1**LA(1)
      PH=-LA(1)
      TOT(2)=1D1**LA(2)
      PE=-LA(2)
C                   RESET TOTAL MOLALITIES
      IF(IMINS.EQ.0) GO TO 320
      DO 340 I=IFT,ILT
      K=IOUT(I)
      TOT(K)=TOT(K)+DELTOT(I)
  340 CONTINUE
C                   TOTAL MINERALS AND THOR
      DO 360 I=IFM,ILM
      K=MAXT+I-ILT
      TOT(K)=TOT(K)+DELTA(I)
      IF(IOPT(3).EQ.6.AND.I.EQ.IFM) THEN
             THOR=THOR+DELTA(I)*THREAC
          ELSE
             THOR=THOR+THMIN(I-ILT)*DELTA(I)
```

```
      END IF
  360 CONTINUE
  320 CONTINUE
      RETURN
      END
      SUBROUTINE PTOT
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      CHARACTER *12 DALK,DN,DN1,DN2,DN3,DNAME
      CHARACTER *80 CARD
      CHARACTER*8 NAMEF(8)
      DATA NAMEF /'OH-', 'O2 AQ', 'H2 AQ', 'HCO3-', 'S-2', 'HS-',
     1    'FE+3', 'Fe+3'/
      DATA NF /8/
      DATA IDATA /0/, DALK/'TOT ALK'/
      DATA DN1/'O2'/,DN2/'H2'/,DN3/'CHARGE'/
      WRITE(IW,220)
      WRITE(IW,230)
      KK=0
      DO 10 I=4,MAXT
      IF (DABS(TOT(I)).LT.1.0D-40) GO TO 10
      KK=1
      DLT=DLOG10(TOT(I))
      DNAME=TNAME(I)
      IF (IASPEC.EQ.I) DNAME=DALK
      WRITE(IW,240) DNAME,TOT(I),DLT
   10 CONTINUE
      IF (KK.EQ.0) WRITE(IW,250)
      WRITE(IW,260)
      RETURN
C     *****
      ENTRY PSPEC
C     *****
      WRITE(IW,270)
      WRITE(IW,280) PH,PE,TOT(3),MU,TC,ELECT,THSOLN,DALKS,ITER
      IF (IASPEC.LE.0) GO TO 20
      WRITE(IW,290) TOTAL(ISOL,IASPEC)
   20 CONTINUE
      IF (IESPEC.LE.1) GO TO 30
      DD=TOT(IESPEC)-DNEUT
      WRITE(IW,300) TNAME(IESPEC),DD
   30 CONTINUE
      WRITE(IW,310)
      LM(1)=LA(1)-LG(1)
      LG(2)=0.0D0
      LM(2)=LA(2)
      LG(3)=0.0D0
      LM(3)=LA(3)
      DO 40 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 40
      DA=0D0
      DM=0D0
      IF (LM(I).LT.-30D0.AND.I.GT.MAXT) GO TO 40
      IF (LM(I).GE.-60D0) DM=1D1**LM(I)
      DLA=LM(I)+LG(I)
      IF (DLA.GE.-60D0) DA=1D1**DLA
      DG=1D1**LG(I)
      IF(I.LE.MAXT) THEN
         GO TO 37
      ELSE
         DO 43 J=1,NF
```

```
         IF (SNAME(I).EQ.NAMEF(J)) GOTO 37
   43    CONTINUE
      END IF
C                                   check that molality > 0.01 of some total
      K=NSP(I)
      DO 35 J=1,K
      IF(LSP(I,J).LT.4) GO TO 35
      IF(CSP(I,J)*DM.GT.0.01*TOT(LSP(I,J))) GO TO 37
   35 CONTINUE
      GO TO 40
   37 CONTINUE
      WRITE(IW,320) I,SNAME(I),ZSP(I),DM,LM(I),DA,DLA,DG,LG(I)
   40 CONTINUE
C     *****
      ENTRY PSUM
C     *****
      IF (NSUMS.EQ.0) GO TO 80
      KK=0
      DO 70 I=1,NSUMS
      LL=0
      DSUM=0D0
      K=NSUM(I)
      DO 50 J=1,K
      IF (SFLAG(LSUM(I,J)).LE.0) GO TO 50
      LL=1
      DSUM=DSUM+M(LSUM(I,J))
   50 CONTINUE
      IF (LL.EQ.0) GO TO 70
      IF (LL.EQ.0.OR.KK.NE.0) GO TO 60
      WRITE(IW,330)
      KK=1
   60 CONTINUE
      WRITE(IW,340) SUNAME(I),DSUM
   70 CONTINUE
   80 CONTINUE
      RETURN
C     *****
      ENTRY PBUG(D,DPHPE)
C     *****
      WRITE(IW,345) ITER,MU
  345 FORMAT(1X,'ITER =',I4,5X,'MU = ',F8.5)
      WRITE(IW,350) D,CR(1),DPHPE
C          PRINT CHANGES IN PH AND PE
      IF (IRS(1).LE.0) GO TO 90
      DPH=-DLOG10(1D0+DELTA(1))
      WRITE(IW,360) PH,DPH
   90 CONTINUE
      IF (IRS(2).LE.0) GO TO 100
      DPE=-DLOG10(1D0+DELTA(IRS(2)))
      WRITE(IW,370) PE,DPE,CR(2)
  100 CONTINUE
C          PRINT TOTALS AND ACTIVITIES
      DO 110 K=4,LASTT
      I=IRS(K)
      IF (I.LE.0) GO TO 110
      AOLD=1D1**LA(K)
      AFACT=1D0+DELTA(I)
      ANEW=AOLD*AFACT
      TOLD=TOT(K)
      TNEW=TOLD+DELTOT(I)
```

```
      WRITE(IW,385) CR(K),TNAME(K),TOLD,TNEW,DELTOT(I),
     1     SNAME(K),AOLD,ANEW,AFACT
  385 FORMAT(1X,1PD8.1,2X,A3,3D9.1,2X,A5,3D9.1)
  110 CONTINUE
C          PRINT MINERAL TOTALS AND DELTAS
      IF (IMINS.LE.0) GO TO 130
      DO 120 I=1,NMINS
      K=MAXT+I
      J=ILT+I
      TNEW=TOT(K)+DELTA(J)
      WRITE(IW,385) CR(K),MNAME(I),TOT(K),TNEW,DELTA(J)
  120 CONTINUE
  130 CONTINUE
      RETURN
C     *****
      ENTRY PPHASE
C     *****
      IF (NMINS.EQ.0) RETURN
      WRITE(IW,400)
      DO 150 I=1,NMINS
      K=NMINO(I)
      DIAP=0.0D0
      DO 140 J=1,K
      DIAP=DIAP+(LG(LMINO(I,J))+LM(LMINO(I,J)))*CMINO(I,J)
  140 CONTINUE
      DSI=DIAP-LKMINO(I)
      K=MAXT+I
      D1=TOT(K)
      IF (IOPT(3).EQ.6.AND.I.EQ.1) D1=0D0
      WRITE(IW,410) MNAME(I),D1,DIAP,LKMINO(I),DSI
      IF (IOPT(3).EQ.6.AND.I.EQ.1) WRITE(IW,420)
  150 CONTINUE
      WRITE(IW,430)
      IF (IOPT(3).EQ.6) WRITE(IW,440) TOT(MAXT+1),MNAME(1)
      IF (IOPT(3).NE.6) RETURN
C     *****
      ENTRY PREAC
C     *****
      WRITE(IW,450)
      DO 160 I=1,NCOMPS
      L=LREAC(I)
      IF (L.EQ.0) DN=DN3
      IF (L.LT.MAXT1) DN=TNAME(L)
      IF (L.GT.MAXT) DN=DN1
      IF (L.GT.MAXT.AND.THMEAN(I).LT.0) DN=DN2
      WRITE(IW,460) CREAC(I),DN,THMEAN(I)
  160 CONTINUE
      RETURN
C     *****
      ENTRY PLOOK
C     *****
      IF (NLOOKS.EQ.0) RETURN
      KK=0
      DO 190 I=1,NLOOKS
      K=NLOOK(I)
      DIAP=0D0
      DO 170 J=1,K
      LL=LLOOK(I,J)
      IF (SFLAG(LL).LE.0) GO TO 190
      DIAP=DIAP+(LG(LL)+LM(LL))*CLOOK(I,J)
```

```
  170 CONTINUE
      IF (KK.NE.0) GO TO 180
      KK=1
      WRITE(IW,470)
  180 CONTINUE
      DSI=DIAP-LKLOOK(I)
      WRITE(IW,480) NAMELK(I),DIAP,LKLOOK(I),DSI
  190 CONTINUE
      RETURN
C     *****
      ENTRY PDATA
C     *****
      IF (IOPT(1).NE.1) RETURN
      IF (IDATA.GT.0) RETURN
      IDATA=1
      REWIND IDB
      WRITE(IW,490)
  200 CONTINUE
      READ(IDB,500,END=210) CARD
      WRITE(IW,510) CARD
      GO TO 200
  210 CONTINUE
      RETURN
C
  220 FORMAT (///24X,'TOTAL MOLALITIES OF ELEMENTS'/,24X,'----- --------
     1-- -- --------')
  230 FORMAT (/16X,'ELEMENT',10X,'MOLALITY',9X,'LOG MOLALITY'/)
  240 FORMAT (16X,A8,6X,1PD13.6,8X,0PF9.4)
  250 FORMAT (16X,'PURE WATER')
  260 FORMAT (//)
  270 FORMAT (//,24X,'----DESCRIPTION OF SOLUTION----')
  280 FORMAT (/,39X,'PH = ',F8.4/39X,'PE = ',F8.4/29X,'ACTIVITY H2O = ',
     1F8.4/27X,'IONIC STRENGTH = ',F8.4/30X,'TEMPERATURE = ',F8.4/23X,'E
     2LECTRICAL BALANCE = ',1PD12.4/37X,'THOR = ',D12.4/25X,'TOTAL ALKAL
     3INITY = ',D12.4/31X,'ITERATIONS = ',0PI3)
  290 FORMAT (29X,'TOTAL CARBON = ',1PD12.4)
  300 FORMAT (20X,'MOLES OF ',A8,' ADDED = ',D12.4)
  310 FORMAT (///,26X,23('-')/26X,'DISTRIBUTION OF SPECIES'/26X,23('-')/
     1/2X,'I',2X,'SPECIES',4X,'Z',3X,'MOLALITY',2X,'LOG MOLAL',3X,'ACTIV
     2ITY',2X,'LOG ACT',4X,'GAMMA',3X,'LOG GAM'/)
  320 FORMAT (1X,I3,1X,A8,1X,F4.1,1X,1PE10.3,2X,0PF7.3,2X,2(1PE10.3,1X,
     10PF7.3,1X))
  330 FORMAT (///25X,'SUMS OF SPECIES'/)
  340 FORMAT (22X,A8,' = ',1PD13.6)
  350 FORMAT (/1X,'REDUCTION FACTOR: ',1PD12.5,3X,'ELECT: ',D12.5,3X,
     1'DPHPE: ',D12.5)
  360 FORMAT (1X,'PH = ',F8.4,5X,'DPH = ',F8.4)
  370 FORMAT (1X,'PE = ',F8.4,5X,'DPE = ',F8.4,5X,'DTHOR = ',1PD12.5)
  380 FORMAT (1X,1PD12.5,1X,A4,1X,D11.4,2(1X,D8.1),1X,A8,1X,D11.4,1X,
     1D8.1)
  390 FORMAT (1X,1PD12.5,1X,A4,1X,D11.4,2(1X,D8.1))
  400 FORMAT (27X,'----PHASE BOUNDARIES----'//,9X,'PHASE',5X,'DELTA PHAS
     1E*',6X,'LOG IAP',6X,'LOG KT',6X,'LOG IAP/KT'/)
  410 FORMAT (8X,A8,2X,1PD13.6,3(4X,0PF9.4))
  420 FORMAT (1H+,5X,'**')
  430 FORMAT (/,1X,'* NEGATIVE DELTA PHASE INDICATES PRECIPITATION',/,3X
     1,'AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.')
  440 FORMAT (/,1X,'** ',1PD12.6,' MOLES OF REACTION',' HAVE BEEN ADDED
     1TO THE SOLUTION',/,4X,'TO REACH THE ',A8,' PHASE BOUNDARY.')
  450 FORMAT (/,6X,'REACTION IS:')
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```
 460 FORMAT (20X,F6.2,' MOLES OF ',A8,'  VALENCE =  ',F6.3)
 470 FORMAT (//28X,'---- LOOK MIN IAP ----'//15X,'PHASE',8X,'LOG IAP',6
     1X,'LOG KT',6X,'LOG IAP/KT'/)
 480 FORMAT (14X,A8,3(4X,F9.4))
 490 FORMAT (1H1,25X,'DATA:  CARD IMAGES FROM DISK'/)
 500 FORMAT (A80)
 510 FORMAT (1X,A80)
      END
      SUBROUTINE READ
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      CHARACTER *12 SUBS,SUB,TNAM,DELETE
      CHARACTER *64 REMRK
      CHARACTER *72 CARD
      DIMENSION ISUB(14),SUBS(14),LT(MAXT),DTOT(MAXT)
      DATA SUBS /'TEMP     ','MINERALS ','SOLUTION ','REACTION ',
     1           'STEPS    ','ELEMENTS ','SPECIES  ','END      ',
     2           'LOOK MIN ','SUMS     ','NEUTRAL  ','KNOBS    ',
     3           'SOLNSAS  ','         '/
      DATA NLKS,NSMS /0,0/
      DATA DELETE /'DELETE   '/
  10 CONTINUE
      IERR=0
      ISOLV(1)=0
      ISOLV(2)=0
      NRMINS=0
      NLOOKS=NLKS
      NSUMS=NSMS
      DO 20 I=1,11
      ISUB(I)=0
  20 CONTINUE
C          READ TITLE CARD
      READ(IR,420,END=410) (TITLE(I),I=1,20)
C          READ OPTION CARD
      READ(IR,430) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO
      IF (IOPT(1).EQ.1) CALL PDATA
      WRITE(IW,440) (TITLE(I),I=1,20)
      WRITE(IW,450) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO
      IREAD=0
      IFILE=IR
      GO TO 30
C     *****
      ENTRY RDATA
C     *****
      WRITE(IW,460)
      IREAD=1
      IFILE=IDB
  30 CONTINUE
C          READ SUBROUTINE CARD AND BRANCH
  40 CONTINUE
      READ(IFILE,470) SUB,ISOLN
      DO 50 I=1,13
      IF (SUB.NE.SUBS(I)) GO TO 50
      GO TO (60,70,110,150,170,180,220,400,260,350,390,1010,1100), I
  50 CONTINUE
      WRITE(IW,480) SUB
      GO TO 40
C
C          READ TEMP DATA
C
  60 CONTINUE
```

```
      WRITE(IW,490)
      IF (IOPT(4).EQ.0) GO TO 40
      NTEMP=IOPT(4)
      IF (NTEMP.EQ.3) NTEMP=NSTEPS
      READ(IFILE,500) (TSTEP(I),I=1,NTEMP)
      WRITE(IW,510) (TSTEP(I),I=1,NTEMP)
      ISUB(1)=1
      GO TO 40
C
C          READ MINERAL DATA
C
   70 CONTINUE
      WRITE(IW,520)
      I=0
   80 CONTINUE
      I=I+1
C          READ NAME ETC. FOR MINERAL
      READ(IFILE,530) MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),
     1MFLAG(I),SIMIN(I)
      WRITE(IW,540) MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),
     1MFLAG(I),SIMIN(I)
      IF (NMINO(I).EQ.0) GO TO 100
      NRMINS=I
C          READ COEFFICIENTS FOR MINERAL
      K=NMINO(I)
      READ(IFILE,550) (LMINO(I,J),CMINO(I,J),J=1,K)
      WRITE(IW,560) (LMINO(I,J),CMINO(I,J),J=1,K)
C          READ ANALYTIC EXPRESSION COEFFICIENTS
      IF (MFLAG(I).EQ.0) GO TO 90
      READ(IFILE,570) (AMIN(I,J),J=1,5)
      WRITE(IW,580) (AMIN(I,J),J=1,5)
   90 CONTINUE
      GO TO 80
  100 CONTINUE
      CALL MINCON
      CALL CHKMIN(IERR)
      ISUB(2)=1
      GO TO 40
C
C          READ A SOLUTION
C
  110 CONTINUE
      WRITE(IW,590) ISOLN
C          READ SOLUTION TITLE
      READ(IFILE,600) (HEAD(ISOLN,J),J=1,20)
      WRITE(IW,610) (HEAD(ISOLN,J),J=1,20)
C          READ NTOTS,PH,EH
      READ(IFILE,620) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),
     1SDENS(ISOLN)
      IF (DABS(SDENS(ISOLN)).LT.1.0D-40) SDENS(ISOLN)=1.0
      WRITE(IW,630) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),
     1SDENS(ISOLN)
C          READ TOTALS
      DO 120 I=1,MAXT
      TOTAL(ISOLN,I)=0D0
  120 CONTINUE
      IF (NTOTS.EQ.0) GO TO 140
      READ(IFILE,640) (LT(J),DTOT(J),J=1,NTOTS)
      WRITE(IW,650) (LT(J),DTOT(J),J=1,NTOTS)
C          ZERO TOTAL AND INSERT VALUES
```

```
      DO 130 I=1,NTOTS
      TOTAL(ISOLN,LT(I))=DTOT(I)
  130 CONTINUE
      CALL UNITS(ISOLN)
  140 CONTINUE
      TOTAL(ISOLN,1)=1D1**(-PH)
      TOTAL(ISOLN,2)=1D1**(-PE)
      ISOLV(ISOLN)=1
      ISUB(3)=1
      GO TO 40
C
C          READ REACTION DATA
C
  150 CONTINUE
      IF (NCOMPS.EQ.0) GO TO 40
      WRITE(IW,660)
C          READ COEFFICIENTS OF REACTION
      READ(IFILE,670) (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)
      WRITE(IW,680) (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)
      THREAC=0D0
      DO 160 I=1,NCOMPS
      THREAC=THREAC+THMEAN(I)*CREAC(I)
  160 CONTINUE
      ISUB(4)=1
      GO TO 40
C
C          READ STEPS DATA
C
  170 CONTINUE
      IF (NSTEPS.EQ.0.OR.IOPT(3).EQ.5) GO TO 40
      WRITE(IW,690)
      K=NSTEPS
      IF (IOPT(3).EQ.4) K=1
      READ(IFILE,700) (XSTEP(I),I=1,K)
      WRITE(IW,710) (XSTEP(I),I=1,K)
      ISUB(5)=1
      GO TO 40
C
C          READ ELEMENT CARDS
C
  180 CONTINUE
      WRITE(IW,720)
C          READ ELEMENTS UNTIL BLANK CARD
  190 CONTINUE
      READ(IFILE,730) TNAM,NELT,TGFW
      IF (IREAD.EQ.0) WRITE(IW,740) TNAM,NELT,TGFW
      IF (NELT.EQ.0) GO TO 210
      IF (NELT.GT.3.AND.NELT.LE.MAXT) GO TO 200
      WRITE(IW,750) NELT,TNAM,SUBS(6)
      ENDFILE (UNIT=IW)
      STOP
  200 CONTINUE
      TNAME(NELT)=TNAM
      GFW(NELT)=TGFW
      GO TO 190
  210 CONTINUE
      ISUB(6)=1
      GO TO 40
C
C          READ SPECIES CARDS
```

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C
  220 CONTINUE
      WRITE(IW,760)
C          READ SPECIES CARDS UNTIL BLANK CARD
  230 CONTINUE
      READ(IFILE,770) I
      IF (IREAD.EQ.0) WRITE(IW,780) I
C          READ SPECIES NAME ETC.
      IF (I.EQ.0) GO TO 250
      IF (I.GT.0.AND.I.LE.MAXS) GO TO 240
      READ(IFILE,790) TNAM
      WRITE(IW,750) I,TNAM,SUBS(7)
      ENDFILE (UNIT=IW)
      STOP
  240 CONTINUE
      READ(IFILE,790) SNAME(I),NSP(I),KFLAG(I),GFLAG(I),ZSP(I),THSP(I),
     1DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)
      IF (IREAD.EQ.0) WRITE(IW,800)SNAME(I),NSP(I),KFLAG(I),GFLAG(I)
     1,ZSP(I),THSP(I),DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)
      IF (NSP(I).EQ.0) GO TO 230
C          READ LOG K DATA FOR SPECIES
      READ(IFILE,810) LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)
      IF (IREAD.EQ.0) WRITE(IW,820) LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)
C          READ COEFFICIENTS
      K=NSP(I)
      READ(IFILE,830) (LSP(I,J),CSP(I,J),J=1,K)
      IF (IREAD.EQ.0) WRITE(IW,840) (LSP(I,J),CSP(I,J),J=1,K)
      GO TO 230
  250 CONTINUE
      ISUB(7)=1
      CALL CHKSPE(IERR)
      GO TO 40
C
C          READ MINERALS TO LOOK AT
C
  260 CONTINUE
      WRITE(IW,850)
      I=NLKS
  270 CONTINUE
      I=I+1
      IF (I.LE.MAXLK) GO TO 280
      WRITE(IW,860) MAXLK
      I=MAXLK
  280 CONTINUE
C          READ NAME ETC.
      READ(IFILE,870) NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK(I),LOOKFL(I)
      IF (IREAD.EQ.0) WRITE(IW,880) NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK
     1(I),LOOKFL(I)
      IF (NAMELK(I).NE.DELETE) GO TO 290
      I=0
      NLOOKS=I
      GO TO 270
  290 CONTINUE
      IF (NLOOK(I).EQ.0) GO TO 340
C          CHECK TO SEE IF MINERAL IS ALREADY IN THE LIST
      IF (I.LE.1) GO TO 310
      L=I-1
      DO 300 N=1,L
      IF (NAMELK(I).NE.NAMELK(N)) GO TO 300
      NLOOK(N)=NLOOK(I)
```

```
      LKOLK(N)=LKOLK(I)
      DHLOOK(N)=DHLOOK(I)
      LOOKFL(N)=LOOKFL(I)
      I=I-1
      GO TO 320
  300 CONTINUE
  310 CONTINUE
      N=I
      NLOOKS=I
C          N IS THE NUMBER FOR THE MINERAL BEING READ.
  320 CONTINUE
C          READ COEFFICIENTS
      K=NLOOK(N)
      READ(IFILE,550) (LLOOK(N,J),CLOOK(N,J),J=1,K)
      IF (IREAD.EQ.0) WRITE(IW,560) (LLOOK(N,J),CLOOK(N,J),J=1,K)
C          READ ANALYTIC EXPRESSION
      IF (LOOKFL(N).EQ.0) GO TO 330
      READ(IFILE,570) (ALOOK(N,J),J=1,5)
      IF (IREAD.EQ.0) WRITE(IW,580) (ALOOK(N,J),J=1,5)
  330 CONTINUE
      GO TO 270
  340 CONTINUE
      NLKS=NLOOKS
      CALL CHKLK
      ISUB(9)=1
      GO TO 40
C
C          READ LISTS FOR SUMS OF SPECIES
C
  350 CONTINUE
      WRITE(IW,890)
      I=NSMS
  360 CONTINUE
      I=I+1
      IF(I.GT.MAXSUM) THEN
         WRITE(IW,365) MAXSUM
  365    FORMAT(' ***** MAXIMUM NUMBER OF SUMS,',I4,', EXCEEDED.  ',
     1   'RECOMPILE WITH LARGER MAXSUM. *****')
         I=MAXSUM
      END IF
      READ(IFILE,900) SUNAME(I),K
      IF (IREAD.EQ.0) WRITE(IW,910) SUNAME(I),K
      IF (SUNAME(I).EQ.DELETE) THEN
         I=0
         NSUMS=0
         GO TO 360
      END IF
      IF (K.GT.0) THEN
         NSUM(I)=K
         NSUMS=I
         READ(IFILE,920) (LSUM(I,J),J=1,K)
         IF (IREAD.EQ.0) WRITE(IW,930) (LSUM(I,J),J=1,K)
         GO TO 360
      END IF
      NSMS=NSUMS
      ISUB(10)=1
      GO TO 40
C
C          READ SPECIES TO ADJUST FOR ELECTRICAL NEUTRALITY
C
```

```
  390 CONTINUE
      WRITE(IW,940)
      READ(IFILE,950) LPOS,LNEG
      WRITE(IW,960) LPOS,LNEG
      ISUB(11)=1
      GO TO 40
C
C                    READ CONVERGENCE PARAMETERS
C
 1010 CONTINUE
      WRITE(IW,1020)
 1020 FORMAT(' KNOBS')
      READ(IFILE,1050) CARD
 1050 FORMAT(A72)
      WRITE(IW,1030) CARD
 1030 FORMAT(1X,A72)
      READ(CARD,*) DMAX,DMIN,FUDGE,RMAX,RMIN,CNVG1,CNVG2,ITMAX,CHKMU
      GO TO 40
 1100 CONTINUE
C
C                    READ SOLUTION DATA GENERATED BY SAS
C
      WRITE(IW,1110) ISOLN
 1110 FORMAT(1X,'SOLNSAS ',I1)
C                    READ SOLUTION TITLE
      READ(IFILE,600) (HEAD(ISOLN,J),J=1,20)
      WRITE(IW,610) (HEAD(ISOLN,J),J=1,20)
C                    READ NTOTS,PH,EH
      READ(IFILE,620) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),
     1SDENS(ISOLN)
      IF(DABS(SDENS(ISOLN)).LT.1.0D-40) SDENS(ISOLN)=1.0
      WRITE(IW,630) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),
     1SDENS(ISOLN)
C                    READ TOTALS
      DO 1130 I=1,MAXT
      TOTAL(ISOLN,I)=0D0
 1130 CONTINUE
      NTOTS=0
 1140 CONTINUE
      READ(IFILE,1150) LTT,DTOTT,REMRK
 1150 FORMAT(I4,D11.3,1X,A64)
      WRITE(IW,1160) LTT,DTOTT,REMRK
 1160 FORMAT(1X,I4,1PD11.3,1X,A64)
      IF(LTT.EQ.0) GO TO 1170
      TOTAL(ISOLN,LTT)=DTOTT
      NTOTS=NTOTS+1
      GO TO 1140
 1170 CONTINUE
      CALL UNITS(ISOLN)
      TOTAL(ISOLN,1)=1D1**(-PH)
      TOTAL(ISOLN,2)=1D1**(-PE)
      ISOLV(ISOLN)=1
      ISUB(3)=1
      GO TO 40
C
C            END DATA ENTRY FOR THIS SIMULATION
C
  400 CONTINUE
      IF (IREAD.EQ.1) RETURN
      IF (IERR.LE.0) GO TO 405
```

```
      ENDFILE (UNIT=IW)
      STOP
  405 IF (IOPT(4).GT.0.AND.ISUB(1).EQ.0) IERR=1
      IF (IOPT(3).GT.0.AND.IOPT(3).LT.5.AND.ISUB(5).EQ.0) IERR=5
      IF (IOPT(3).GE.3.AND.IOPT(3).LT.5.AND.ISUB(4).EQ.0) IERR=4
      IF (IOPT(3).EQ.5.AND.ISUB(2).EQ.0) IERR=2
      IF (IOPT(3).EQ.6.AND.ISUB(2).EQ.0) IERR=2
      IF (IOPT(3).EQ.6.AND.ISUB(4).EQ.0) IERR=4
      IF (IOPT(2).EQ.2.AND.ISUB(11).EQ.0) IERR=11
      IF (IERR.EQ.0) RETURN
      WRITE(IW,970) SUBS(IERR)
      IF (IOPT(7).EQ.0) GO TO 10
  410 CONTINUE
      ENDFILE (UNIT=IW)
      STOP
C
  420 FORMAT (20A4)
  430 FORMAT (10I1,I2,I2,6X,F10.5)
  440 FORMAT (1H1,20A4)
  450 FORMAT (1X,10I1,I2,I2,6X,F10.5)
  460 FORMAT (10X,'DATA READ FROM DISK'/)
  470 FORMAT (A8,1X,I1)
  480 FORMAT (1X,'** ',A8,' **  INPUT UNKNOWN')
  490 FORMAT (1X,'TEMP')
  500 FORMAT (8F10.1)
  510 FORMAT (1X,8G10.3)
  520 FORMAT (1X,'MINERALS')
  530 FORMAT (A8,2X,I2,3X,3F10.2,5X,I1,9X,F10.3)
  540 FORMAT (1X,A8,2X,I2,3X,3G10.2,5X,I1,9X,F10.3)
  550 FORMAT ((5(I4,F11.3)))
  560 FORMAT ((1X,5(I4,G11.3)))
  570 FORMAT (5E12.5)
  580 FORMAT (1X,1P5E12.4)
  590 FORMAT (1X,'SOLUTION ',I1)
  600 FORMAT (20A4)
  610 FORMAT (1X,20A4)
  620 FORMAT (I2,I3,I2,3X,4F10.0)
  630 FORMAT (1X,I2,I3,I2,3X,4G10.3)
  640 FORMAT ((5(I4,D11.3)))
  650 FORMAT ((1X,5(I4,1PD11.3)))
  660 FORMAT (1X,'REACTION')
  670 FORMAT ((4(I4,2F8.3)))
  680 FORMAT ((1X,4(I4,2F8.3)))
  690 FORMAT (1X,'STEPS')
  700 FORMAT (8F10.3)
  710 FORMAT (1X,8G10.3)
  720 FORMAT (1X,'ELEMENTS')
  730 FORMAT (A9,1X,I2,3X,F10.0)
  740 FORMAT (1X,A9,2X,I2,3X,E16.5)
  750 FORMAT (1X,I4,2X,A8,5X,A8,' INDEX NUMBER IS OUT OF RANGE.'//1X,'CA
     1LCULATION TERMINATED.')
  760 FORMAT (1X,'SPECIES')
  770 FORMAT (I3)
  780 FORMAT (1X,I3)
  790 FORMAT (A8,2X,I3,I1,I1,6F10.3)
  800 FORMAT (1X,A8,2X,I3,I1,I1,6F10.3)
  810 FORMAT (2F10.3,5E12.5)
  820 FORMAT (1X,2F10.3,5G12.5)
  830 FORMAT (6(I3,F7.3))
  840 FORMAT ((1X,6(I3,F7.3)))
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```
  850 FORMAT (1X,'LOOK MIN')
  860 FORMAT (1X,'***** LOOK MIN ARRAY ALREADY HAS',I5,' MINERALS.',
     1    'RECOMPILE WITH LARGER MAXLK.  *****')
  870 FORMAT (A8,2X,I2,13X,2F10.2,5X,I1)
  880 FORMAT (1X,A8,2X,I2,13X,2G10.3,5X,I1)
  890 FORMAT (1X,'SUMS')
  900 FORMAT (A8,2X,I2)
  910 FORMAT (1X,A8,2X,I2)
  920 FORMAT (20I4)
  930 FORMAT (1X,20I4)
  940 FORMAT (1X,'NEUTRAL')
  950 FORMAT (2I5)
  960 FORMAT (1X,2I5)
  970 FORMAT (//1X,14('*')/1X,'TERMINAL ERROR  INPUT LACKED ',A8,' CARDS
     1'/1X,14('*'))
      END
      SUBROUTINE INOUT
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C
C          DETERMINE TOTALS TO BE INCLUDED AS EQUATIONS IN MATRIX.
C
      DO 10 I=4,MAXT
      IIN(I)=0
      IF (TOT(I).LE.0.0D0) GO TO 10
      IIN(I)=1
   10 CONTINUE
      LAST=0
      LASTT=0
      DO 20 I=1,MAXT
      IF (IIN(I).EQ.0) GO TO 20
      LAST=LAST+1
      IIN(I)=LAST
      LASTT=I
      IOUT(LAST)=I
   20 CONTINUE
      ILT=LAST
C          PICK SPECIES TO BE INCLUDED
      IF (LASTT.LT.4) LASTT=4
      SFLAG(1)=1
      SFLAG(2)=1
      SFLAG(3)=1
      DO 30 I=4,MAXT
      SFLAG(I)=0
      IF (IIN(I).GT.0) SFLAG(I)=1
   30 CONTINUE
      DO 50 I=MAXT1,MAXS
      SFLAG(I)=0
      K=NSP(I)
      IF (K.EQ.0) GO TO 50
      DO 40 J=1,K
      IF (SFLAG(LSP(I,J)).LE.0) GO TO 50
   40 CONTINUE
      SFLAG(I)=1
      LASTS=I
   50 CONTINUE
C          ZERO ARRAY AR
      DO 70 I=1,MAXEQ
      DO 60 J=1,MAXEQ
      AR(I,J)=0D0
   60 CONTINUE
```

```
   70 CONTINUE
C           PUT MINERAL COEFFICIENTS INTO FULL ARRAY
      IF (NMINS.LE.0) GO TO 120
      DO 90 I=1,NMINS
      K=NMIN(I)
      L=MAXT+I
      DO 80 J=1,K
      K1=LMIN(I,J)
      AR(K1,L)=-CMIN(I,J)
      AR(L,K1)=CMIN(I,J)
   80 CONTINUE
      AR(1,L)=0D0
      AR(2,L)=-THMIN(I)
   90 CONTINUE
      IF (IOPT(3).NE.6) GO TO 120
C           ADD REACTION TO EQUILBRATE WITH MINERAL # 1.
      L=MAXT+1
      DO 100 I=1,MAXT
      AR(I,L)=0D0
  100 CONTINUE
      DO 110 I=1,NCOMPS
      J=LREAC(I)
      AR(J,L)=AR(J,L)-CREAC(I)
      AR(2,L)=AR(2,L)-CREAC(I)*THMEAN(I)
  110 CONTINUE
  120 CONTINUE
      RETURN
      END
      SUBROUTINE KTEMP
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      DATA C/2.302585092/,R/1.98719D-3/
C
C           COMPUTE TEMPERATURE DEPENDENCE OF A AND B FOR DEBYE-HUCKEL
C
      S1=374.11-TC
      S2=S1**0.33333333
      S3=1.0+0.1342489*S2-3.946263E-03*S1
      S3=S3/(3.1975-0.3151548*S2-1.203374E-03*S1+7.48908E-13*S1**4.0)
      S3=DSQRT(S3)
      IF (TK.LT.373.15) GO TO 10
      C1=5321.0/TK+233.76-TK*(TK*(8.292E-07*TK-1.417E-03)+0.9297)
      GO TO 20
   10 C1=87.74-TC*(TC*(1.41E-06*TC-9.398E-04)+0.4008)
   20 CONTINUE
      C1=DSQRT(C1*TK)
      A=1824600.0*S3/C1**3.0
      B=50.29*S3/C1
C
C           COMPUTE VANT HOFF CONSTANTS
C
      C1=(298.15-TK)/(298.15*TK*C*R)
      DO 30 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 30
      IF (KFLAG(I).EQ.1) LKSP(I)=ASP(I,1)+ASP(I,2)*TK+ASP(I,3)/TK+ASP(I,
     14)*DLOG10(TK)+ASP(I,5)/TK**2D0
      IF (KFLAG(I).EQ.0) LKSP(I)=LKTOSP(I)-DHSP(I)*C1
   30 CONTINUE
      IF (NLOOKS.EQ.0) GO TO 50
      DO 40 I=1,NLOOKS
      IF (LOOKFL(I).EQ.0) LKLOOK(I)=LKOLK(I)-DHLOOK(I)*C1
```

```
      IF (LOOKFL(I).EQ.1) LKLOOK(I)=ALOOK(I,1)+ALOOK(I,2)*TK+ALOOK(I,3)/
     1TK+ALOOK(I,4)*DLOG10(TK)+ALOOK(I,5)/TK**2D0
   40 CONTINUE
   50 CONTINUE
      RETURN
C     *****
      ENTRY KMIN
C     *****
      IF (NMINS.EQ.0) GO TO 80
      DO 70 I=1,NMINS
      IF (MFLAG(I).EQ.0) LKMIN0(I)=LKTOM(I)-DHMIN(I)*C1
      IF (MFLAG(I).EQ.1) LKMIN0(I)=AMIN(I,1)+AMIN(I,2)*TK+AMIN(I,3)/TK+A
     1MIN(I,4)*DLOG10(TK)+AMIN(I,5)/TK**2D0
C           CONVERT K TO MASTER SPECIES
      LKMIN(I)=LKMIN0(I)+SIMIN(I)
      IF (NMCON(I).EQ.0) GO TO 70
      K=NMCON(I)
      DO 60 J=1,K
      LKMIN(I)=CMCON(I,J)*LKSP(LMCON(I,J))+LKMIN(I)
   60 CONTINUE
   70 CONTINUE
   80 CONTINUE
      RETURN
      END
      SUBROUTINE MINCON
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C           LOOP ON NUMBER OF MINERALS
      DO 100 I=1,NRMINS
      K=NMIN0(I)
      ICOMP=0
      NONMAS=0
C           LOOP ON INDIVIDUAL MINERAL
      DO 90 J=1,K
      IF (LMIN0(I,J).GT.MAXT) GO TO 40
      IF (ICOMP.EQ.0) GO TO 20
C           CHECK TO SEE IF COMPONENT IS ALREADY IN LIST
      DO 10 I1=1,ICOMP
      IF (LMIN(I,I1).EQ.LMIN0(I,J)) GO TO 30
   10 CONTINUE
   20 CONTINUE
C           COMPONENT NOT IN LIST
      ICOMP=ICOMP+1
      LMIN(I,ICOMP)=LMIN0(I,J)
      CMIN(I,ICOMP)=CMIN0(I,J)
      GO TO 90
C          COMPONENT ALREADY IN LIST
   30 CONTINUE
      CMIN(I,I1)=CMIN(I,I1)+CMIN0(I,J)
      GO TO 90
C           COMPONENT MUST BE REDUCED TO MASTER SPECIES
   40 CONTINUE
      J1=LMIN0(I,J)
      K1=NSP(J1)
      NONMAS=NONMAS+1
      LMCON(I,NONMAS)=J1
      CMCON(I,NONMAS)=-CMIN0(I,J)
C           LOOP THROUGH MASTER SPECIES OF NON-MASTER SPECIES COMPONENT
      DO 80 I1=1,K1
      IF (ICOMP.EQ.0) GO TO 60
      DO 50 L1=1,ICOMP
```

```
      IF (LSP(J1,I1).EQ.LMIN(I,L1)) GO TO 70
   50 CONTINUE
C          MASTER SPECIES NOT IN LIST
   60 CONTINUE
      ICOMP=ICOMP+1
      LMIN(I,ICOMP)=LSP(J1,I1)
      CMIN(I,ICOMP)=CMINO(I,J)*CSP(J1,I1)
      GO TO 80
C          MASTER SPECIES IN LIST
   70 CONTINUE
      CMIN(I,L1)=CMIN(I,L1)+CMINO(I,J)*CSP(J1,I1)
   80 CONTINUE
C          END LOOP MASTER SPECIES OF NON MASTER SPECIES COMPONENT
   90 CONTINUE
      NMIN(I)=ICOMP
      NMCON(I)=NONMAS
C          END LOOP ON SINGLE MINERAL
  100 CONTINUE
C          END ALL MINERALS
      RETURN
      END
      SUBROUTINE PICK1
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
C
C          THIS SUBROUTINE CHOOSES THE MODEL FOR THE INITIAL SOLUTIONS
C
      DZOFF=0D0
      IIN(1)=1
      IIN(2)=0
      IIN(3)=0
      NMINS=0
      IFE=1
      ILE=1
      IF (IESPEC.EQ.1) GO TO 10
      IIN(1)=0
      IFE=0
      ILE=0
   10 CONTINUE
C          CHECK ALKALINITY TOTAL
      DALKT=0D0
      IASPEC=IALK(ISOL)
      IF (IASPEC.EQ.0) GO TO 30
      IF (TOTAL(ISOL,IASPEC).GT.0D0) GO TO 20
      WRITE(IW,140)
      ENDFILE (UNIT=IW)
      STOP
   20 CONTINUE
      DALKT=TOTAL(ISOL,IASPEC)
      IF (IESPEC.EQ.0.OR.IESPEC.NE.IASPEC) GO TO 30
      WRITE(IW,150)
      ENDFILE (UNIT=IW)
      STOP
   30 CONTINUE
      DNEUT=0.0D0
      IF (IESPEC.LT.4) GO TO 40
C          MAKE SURE NEUTRAL SPECIES .GT. 0
      DNEUT=TOT(IESPEC)
      IF (TOT(IESPEC).LE.0D0) TOT(IESPEC)=1D-3
   40 CONTINUE
      CALL INOUT
```

```
C          SET COUNTERS ON THE ARRAY
      IFTH=0
      ILTH=0
      IFT=ILE+1
      ILT=ILT
      IFM=0
      ILM=0
      NEQ=ILT
      NEQ1=NEQ+1
      RETURN
C     *****
      ENTRY PICK2
C     *****
C
C          THIS SUBROUTINE CHOOSES THE MODEL FOR THE REACTION SOLUTIONS
C
      IIN(1)=1
      IIN(2)=0
      IF (IOPT(5).GT.0) IIN(2)=1
      IIN(3)=0
      IESPEC=1
      IASPEC=0
      NMINS=NRMINS
C          ADD IN ANY MINERALS NOT INCLUDED IN TOTALS
      IF (NMINS.EQ.0) GO TO 110
      TOT(3)=1D0
      ICK=0
      DO 50 I=1,NMINS
      TOT(MAXT+I)=0D0
   50 CONTINUE
   55 CONTINUE
C          CHECK TO MAKE SURE NECESSARY TOTALS > 0.
      JCK=0
      ICK=ICK+1
      DO 70 I=1,NMINS
      IF (IOPT(3).EQ.6.AND.I.EQ.1) GO TO 70
      K=NMIN(I)
C          IF TOTALS > 0 NEXT MINERAL
      DO 60 J=1,K
      IF (LMIN(I,J).LT.4) GO TO 60
      IF(TOT(LMIN(I,J)).GT.0D0) GO TO 60
      GO TO 65
   60 CONTINUE
      GO TO 70
   65 CONTINUE
C          SOME TOTAL <= 0.  IF ALL CMIN > 0 ADD MINERAL.
      DO 75 J=1,K
      IF (LMIN(I,J).LT.4) GO TO 75
      IF (CMIN(I,J).GT.0) GO TO 75
      GO TO 85
   75 CONTINUE
      D=1D-6
C          ADD D OF MINERAL # I.
   95 CONTINUE
      TOT(MAXT+I)=D
      THOR=THOR+THMIN(I)*D
      DO 105 J=1,K
      K1=LMIN(I,J)
      IF(K1.LT.4)GO TO 105
      TOT(K1)=TOT(K1)+D*CMIN(I,J)
```

```
  105 CONTINUE
      GO TO 70
C          SOME TOTAL <= 0.  CHECK IF TOTALS <= 0 HAVE SAME SIGN FOR CMI
   85 CONTINUE
      NCNEG=0
      NCPOS=0
      D=1D1
      DO 115 J=1,K
      K1=LMIN(I,J)
      D1=TOT(K1)
      IF (D1.LE.0D0) GO TO 125
      IF (D1.LT.D) D=D1
      GO TO 115
  125 CONTINUE
      IF(CMIN(I,J).LE.0D0) NCNEG=1
      IF(CMIN(I,J).GT.0D0) NCPOS=1
  115 CONTINUE
      IF(NCNEG.GT.0.AND.NCPOS.GT.0) GO TO 135
      D=D/5D1
      IF(NCNEG.EQ.1) D=-D
      GO TO 95
  135 CONTINUE
      JCK=1
   70 CONTINUE
      IF(JCK.EQ.0) GO TO 145
      IF(ICK.LE.NMINS+1) GO TO 55
      WRITE(IW,155)
  155 FORMAT(1H1,90('*')/'I HAD TROUBLE ADDING MINERALS SO THAT',
     1      ' ALL THE NECESSARY ELEMENTS HAD POSITIVE CONCENTRATIONS.'/
     2      'PLEASE ADJUST INITIAL CONCENTRATIONS TO SOME SMALL ',
     3      'POSITIVE QUANTITY.'/90('*'))
      ENDFILE (UNIT=IW)
      STOP
  145 CONTINUE
C          ADD ANY REACTION ELEMENTS IF IOPT(3)=6.
      IF (IOPT(3).NE.6) GO TO 100
      DO 90 I=1,NCOMPS
      IF (TOT(LREAC(I)).GT.0D0) GO TO 90
      D=DSIGN(1D-6,CREAC(I))
      TOT(MAXT1)=D
      DO 80 J=1,NCOMPS
      THOR=THOR+CREAC(J)*THMEAN(J)*D
      TOT(LREAC(J))=TOT(LREAC(J))+CREAC(J)*D
   80 CONTINUE
      GO TO 100
   90 CONTINUE
  100 CONTINUE
      TOT(1)=1D1**(-PH)
      TOT(2)=1D1**(-PE)
      TOT(3)=1D0
  110 CONTINUE
      CALL INOUT
C          SET COUNTERS FOR ARRAY
      IFE=1
      ILE=1
      LAST=1
      IFTH=0
      ILTH=0
      IF (IIN(2).LE.0) GO TO 120
      IFTH=2
```

```
      ILTH=2
      LAST=2
  120 CONTINUE
      IFT=LAST+1
      ILT=ILT
      IFM=0
      ILM=0
      NEQ=ILT
      IF (NMINS.EQ.0) GO TO 130
      IFM=ILT+1
      ILM=ILT+NMINS
      NEQ=ILM
  130 CONTINUE
      NEQ1=NEQ+1
      RETURN
C
  140 FORMAT (1X,'CARBON WAS SPECIFIED AS ALKALINITY BUT WAS LESS ','THA
     1N OR EQUAL 0.0.'/1X,'CALCULATIONS TERMINATED')
  150 FORMAT (1X,'ALKALINITY SPECIES CAN NOT BE THE SAME AS THE ','NEUTR
     1AL SPECIES'/1X,'CALCULATIONS TERMINATED')
      END
      SUBROUTINE THORIT(T)
      INCLUDE 'PHREEQE.COMMON.BLOCKS'
      T=0.0D0
      DALKS=0D0
      DO 10 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 10
      DALKS=DALKS+M(I)*ALKSP(I)
      T=T+M(I)*THSP(I)
   10 CONTINUE
      RETURN
C     *****
      ENTRY SOLN
C     *****
      WRITE(IW,260) ISOL,(HEAD(ISOL,I),I=1,20)
      DO 20 I=1,MAXT
      TOT(I)=TOTAL(ISOL,I)
   20 CONTINUE
      THOR=0.0D0
      TC=TEMP(ISOL)
      TK=TC+273.15
      PH=-DLOG10(TOT(1))
      PE=-DLOG10(TOT(2))
      RETURN
C     *****
      ENTRY SAVE
C     *****
      IF (IOPT(7).EQ.0) RETURN
      K=IOPT(7)
      DO 30 I=1,MAXT
      TOTAL(K,I)=TOT(I)
   30 CONTINUE
      TEMP(K)=TC
      TH(K)=THOR
      DIFFZ(K)=DZOFF
      RETURN
C     *****
      ENTRY CHKSPE (IERR1)
C     *****
C          CHECK MASTER SPECIES IN AQUEOUS SPECIES
```

```
      DO 80 I=1,MAXS
      IF (NSP(I).LE.0) GO TO 80
      K=NSP(I)
      DO 70 J=1,K
      L=LSP(I,J)
      IF (L.GE.1.AND.L.LE.MAXT) GO TO 70
      WRITE(IW,270) I,SNAME(I)
      IERR1=1
   70 CONTINUE
   80 CONTINUE
C          CHECK SPECIES
      DO 100 I=MAXT1,MAXS
      K=NSP(I)
      IF (K.EQ.0) GO TO 100
      Z=0.0D0
      DO 90 J=1,K
      Z=Z+ZSP(LSP(I,J))*CSP(I,J)
   90 CONTINUE
      IF (DABS(ZSP(I)-Z).LT.1D-5) GO TO 100
      IERR1=1
      WRITE(IW,280) I,SNAME(I)
  100 CONTINUE
      RETURN
C     *****
      ENTRY CHKMIN (IERR2)
C     *****
C          CHECK MINERALS FOR CHARGE AND VALENCE
      IF (NRMINS.EQ.0) GO TO 140
      THSP(2)=-1D0
      DO 130 I=1,NRMINS
      K=NMINO(I)
      Z=0.0D0
      THR=0.0D0
      DO 110 J=1,K
      Z=Z+ZSP(LMINO(I,J))*CMINO(I,J)
      THR=THR+THSP(LMINO(I,J))*CMINO(I,J)
  110 CONTINUE
      IF (DABS(Z).LT.1D-5) GO TO 120
      IERR2=2
      WRITE(IW,290) I,MNAME(I)
  120 CONTINUE
      IF (DABS(THR-THMIN(I)).LT.1D-5) GO TO 130
      IERR2=3
      WRITE(IW,300) I,MNAME(I)
  130 CONTINUE
      THSP(2)=0D0
  140 CONTINUE
      RETURN
C     *****
      ENTRY CHKLK
C     *****
C          CHECK LOOK MINERALS
      IF (NLOOKS.EQ.0) GO TO 170
      DO 160 I=1,NLOOKS
      K=NLOOK(I)
      Z=0.0D0
      DO 150 J=1,K
      Z=Z+ZSP(LLOOK(I,J))*CLOOK(I,J)
  150 CONTINUE
      IF (DABS(Z).LT.1D-5) GO TO 160
```

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      WRITE(IW,310) I,NAMELK(I)
  160 CONTINUE
  170 CONTINUE
      RETURN
C     *****
      ENTRY UNITS(ISOLN)
C     *****
      IASPEC=IALK(ISOLN)
      IF (IUNITS(ISOLN).EQ.0) GO TO 250
      IF (IUNITS(ISOLN).NE.1) GO TO 190
C          MMOLES/L
      DO 180 I=4,MAXT
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)*GFW(I)
  180 CONTINUE
      IUNITS(ISOLN)=2
  190 CONTINUE
      IF (IUNITS(ISOLN).NE.2) GO TO 210
C          MG/L
      DO 200 I=4,MAXT
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)/SDENS(ISOLN)
  200 CONTINUE
      IUNITS(ISOLN)=3
  210 CONTINUE
      IF (IUNITS(ISOLN).NE.3) GO TO 256
C          PPM
      TOTMG=0.0D0
      DO 220 I=4,MAXT
      TOTMG=TOTMG+TOTAL(ISOLN,I)
  220 CONTINUE
      C=1.0-TOTMG*1E-06
      IF (C.GT.0.0) GO TO 230
      WRITE(IW,320)
      ENDFILE (UNIT=IW)
      STOP
  230 CONTINUE
      C=1.0/(C*1E+03)
      DO 240 I=4,MAXT
      IF (TOTAL(ISOLN,I).LE.0.0D0) GO TO 240
      TOTAL(ISOLN,I)=C*TOTAL(ISOLN,I)/GFW(I)
  240 CONTINUE
      GO TO 250
  256 CONTINUE
      IF(IUNITS(ISOLN).NE.4) GO TO 400
C     MMOL/KG SOLN
      DO 257 I=4,MAXT
      IF(TOTAL(ISOLN,I).LE.0.0D0) GO TO 257
      TOTAL(ISOLN,I) = TOTAL(ISOLN,I)*GFW(I)
  257 CONTINUE
C     NOW IN PPM
      IUNITS(ISOLN)=3
      GO TO 210
  400 WRITE(IW,410)
      ENDFILE (UNIT=IW)
      STOP
  250 CONTINUE
C          UNITS ARE NOW MOLALITY
      RETURN
C
  260 FORMAT (1H1,'SOLUTION NUMBER ',I1,/,1X,20A4/)
  270 FORMAT (1X,I4,2X,A8,5X,'SPECIES HAS A MASTER SPECIES NUMBER OUT OF
```

```
   1        RANGE')
280 FORMAT (1H ,'***** ERROR IN SPECIES NUMBER',I4,'   ',A8,'REACTION D
   1OES NOT CHARGE BALANCE.')
290 FORMAT (1H ,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION DO
   1ES NOT CHARGE BALANCE.')
300 FORMAT (1H ,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION',
   1/,7X,'DOES NOT BALANCE THE SPECIFIED VALENCE.')
310 FORMAT (1H ,'***** WARNING:  LOOK MINERAL NUMBER',I4,2X,A8,' REACT
   1ION',/,7X,'DOES NOT CHARGE BALANCE.')
320 FORMAT (1H1,80('*')//'TERMINAL ERROR'/'TOTAL SALT PPM GREATER ','T
   1HAN 1 MILLION.'/'CHECK CONCENTRATION UNITS AND ELEMENT',' GRAM FOR
   2MULA WEIGHT INPUT',//,1X,80('*'))
410 FORMAT(///,10X,'*** TERMINAL ERROR **** UNITS OF CONCENTRATION UNK
   1NOWN',///)
    END
    SUBROUTINE ZEROAR
    INCLUDE 'PHREEQE.COMMON.BLOCKS'
    IF (IESPEC.GE.2) IIN(1)=1
    IIN(3)=1
    DO 60 I=1,LASTT
    CALCT(I)=0D0
    IF (IIN(I).EQ.0.AND.ITER.GT.1) GO TO 50
    DO 40 J=1,LASTT
    AR(I,J)=0.0D0
 40 CONTINUE
 50 CONTINUE
 60 CONTINUE
    IF (IESPEC.GE.2) IIN(1)=0
    IIN(3)=0
    RETURN
    END
```

Common Blocks for INCLUDE Statements in Source Code

```
 IMPLICIT DOUBLE PRECISION(A-H,O-Z),INTEGER(I-N)
 PARAMETER (MAXT=30,MAXS=250,MAXM=20,MAXLK=200,MAXSUM=10,
1        MXINSM=50)
 PARAMETER (IR=5,IW=6,IDB=11)
 PARAMETER (MAXT1=MAXT+1,MAXEQ=MAXT+MAXM)
 DOUBLE PRECISION LM,M,LA,LG,LKSP,LKMIN,MU
 COMMON /REAL8/ LM(MAXS),M(MAXS),LA(MAXS),LG(MAXS),LKSP(MAXS),
1        TOT(MAXEQ),DELTA(MAXEQ),DELTOT(MAXEQ),
2        AR(MAXEQ,MAXEQ),AS(MAXEQ,MAXEQ),CR(MAXEQ),CS(MAXEQ),
3        LKMIN(MAXM),THOR,ELECT,THSOLN,PH,
4        PE,A,B,MU,TOTAL(2,MAXT),DALKT,DALKS,DIFFZ(2),DZOFF
 DOUBLE PRECISION LKTOSP,LKTOM,LKMINO
 COMMON /REAL4/ CSP(MAXS,6),ZSP(MAXS),THSP(MAXS),LKTOSP(MAXS),
1        DHSP(MAXS),ASP(MAXS,5),ADHSP(MAXS,2),TH(2),
2        TEMP(2),CMIN(MAXM,10),THMIN(MAXM),LKTOM(MAXM),
3        DHMIN(MAXM),AMIN(MAXM,5),CMCON(MAXM,5),CMINO(MAXM,10),
4        LKMINO(MAXM),VO,TK,TC,XSTEP(50),TSTEP(50),CREAC(MAXT),
5        THREAC,THMEAN(MAXT),DHA(MAXS),ALKSP(MAXS),
6        SDENS(2),GFW(MAXT)
 INTEGER GFLAG,SFLAG
 COMMON /INT2/ NSP(MAXS),LSP(MAXS,6),KFLAG(MAXS),GFLAG(MAXS),
1        SFLAG(MAXS),LASTT,LASTS,IIN(MAXEQ),IOUT(MAXEQ),IFE,ILE,
2        IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
3        NMIN(MAXM),LMIN(MAXM,10),MFLAG(MAXM),LMCON(MAXM,5),
4        NMCON(MAXM),LMINO(MAXM,10),NMINO(MAXM),IOPT(10),NMINS,
5        NSTEPS,NCOMPS,NELTS,NSPECS,ISTEP,LREAC(MAXT),
6        NRMINS,ITER,JTER,ISOL,IASPEC,IALK(2),IUNITS(2)
 DOUBLE PRECISION LKLOOK,LKOLK
 COMMON /LOOK/ LKOLK(MAXLK),LKLOOK(MAXLK),
1        DHLOOK(MAXLK),ALOOK(MAXLK,5),CLOOK(MAXLK,10),
2        LLOOK(MAXLK,10),NLOOK(MAXLK),LOOKFL(MAXLK),NLOOKS
 COMMON /NEUT/ DNEUT,NSUM(MAXSUM),NSUMS,LSUM(MAXSUM,MXINSM),
1        LPOS,LNEG
 COMMON /OFFSET/ SIMIN(MAXM),CALCT(MAXEQ)
 COMMON /SWITCH/IRS(MAXEQ),ISR(MAXEQ),NRS,NSR,NFT,NLT,IMINS,
1        JCHECK,ICHECK
 COMMON /KNOBS/ DMAX,DMIN,FUDGE,RMAX,RMIN,CNVG1,CNVG2,ITMAX,CHKMU
 CHARACTER *4 TITLE,HEAD
 CHARACTER *12 SNAME,TNAME,MNAME,NAMELK,SUNAME(MAXSUM)
 COMMON /CHARS/ HEAD(2,20),MNAME(MAXM),NAMELK(MAXLK),SNAME(MAXS),
1        SUNAME,TITLE(20),TNAME(MAXT)
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