Users Guide for
CHIM-XPT: A Program for Computing
Reaction Processes in Aqueous-Mineral-Gas Systems
and
MINTAB Guide

Version 2.50

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FOREWORD

Program CHIM-XPT ("CHIM", for short, herein) is the most advanced member in a series of programs that we have been developing since the mid-1970's for calculating equilibria in aqueous systems (see history, below). CHIM computes simultaneous equilibrium among an minerals, gases and an aqueous phase under conditions of changing composition (X), pressure (P), and temperature (T), thus "CHIM-XPT". Although CHIM and its ancestors were developed for modeling the geochemistry of hydrothermal processes, it applies to any problem that involves calculating states of equilibrium or partial equilibrium in gas-solid-aqueous systems. Example applications include calculations of the following:

- Boiling geothermal waters, producing scale or vein minerals
- Cooling of hydrothermal fluids, yielding vein minerals
- Reaction of fluids with wall rock yielding hydrothermal alteration (seawater-basalt reaction, magmatic water-granite reaction, acidic water reaction with rhyolite)
- Adiabatic decompression of magmatic waters, producing fracture-filling minerals
- Ground water mixing with hot waters, resulting in mineral precipitation
- Mixing of descending acidic waters with ascending neutral-pH waters, resulting in mineral precipitation and evolution of gases
- Reaction of freshwater or seawater with ultramafic rocks, yielding serpentinites plus hyper-alkaline waters bubbling with H_2
- Weathering of basalt and granite under oxidizing conditions
- Reduction of metal-bearing waters by reaction with carbon or methane
- Dolomitization of limestone
- Diagenesis of arkosic sand by reaction of seawater with detrital minerals
- Condensation of hydrothermal gases to form an H_2O-dominated liquid, then oxidation to form sulfuric acid

Engineering applications have included calculations such as the following:

- Re-injection of geothermal waters or gases causing aquifer scaling and permeability loss
- Evolution of CO_2 from oil field waters producing carbonate scale around well bores
- Modeling acidification of geothermal waters to control scale
- Computing reactions between "sequestered" CO_2 and the cement plugging the CO_2 injection wells
- Reaction of mine waste with rain and air
- Reactions of ground water with host rock where it boils around the Yucca Mountain nuclear waste repository
- Scaling of two-phase lines in geothermal settings where two fluids mix or boil

CHIM is a sophisticated program for computing complex chemical processes. It is most successful in the hands of those who apply a good working knowledge of the chemistry of aqueous systems to set up runs to evaluate well-formulated chemical hypotheses. We commonly make six or ten runs on a single problem to evaluate an idea, changing the input between runs on the basis of the previous results.

Although we have made CHIM "friendly", users should recognize that the nature of the problem of solving heterogeneous chemical equilibria under conditions of changing composition, temperature, pressure, enthalpy and simultaneous combinations of these is inherently quite difficult. Even though we have programmed around many kinds of numerical complications, we

cannot “program away” all of the multitude of confounding twists that can arise when solving heterogeneous equilibrium problems. Nevertheless, in our experience we have found very few numerical knots that we could not untie using the methods described in this manual. The most twisted knots are tied to solid solutions. Beginners will find it much more satisfying to avoid solid solutions (set limsol to 0).

A quality thermodynamic data base such as SOLTHERM-XPT is central to meaningful model calculations. We have endeavored to make SOLTHERM-XPT accurate, large and current, but the task of making it comprehensive enough to treat everyone's chemical problems is enormous. We hope users will add new or improved quality data to their own versions of the SOLTHERM data base, including appropriate documentation. Then, to the extent that it is practicable, it would be a tremendous help to all, if users could send their improvements to me from time to time for likely incorporation into the master data base. I also welcome and encourage all users to notify me about problems (bugs or errors) in CHIM and SOLTHERM so that they can be corrected.

CHIM history. CHIM evolved from CHILLER, which evolved from SOLVEQ, all starting in the mid-1970's. SOLVEQ was and is a program for calculating the distribution of aqueous species and mineral saturation indices in natural waters. SOLVEQ gave rise to MINSOLV, a program for computing mineral-gas-aqueous equilibria under conditions of changing composition, usually organized as the titration of a rock into the aqueous phase. MINSOLV begot CHILLER, which was for calculating the cooling of an aqueous phase (thus the name, CHILLER). Since 1976, CHILLER was expanded to include capabilities for mixing of fluids of different temperature, computing boiling and condensation processes using an internal enthalpy equation; finally, the rock titration capability of MINSOLV was incorporated into CHILLER, rendering MINSOLV obsolete. In the 2006-2009 time interval, CHILLER morphed to CHIM-XPT, which includes all of what was CHILLER, but now adds a substantial new dimension – computation of reactions through continuous variations in pressure up to 5kb coupled with a new temperature range up to 600°C (from 350°C). Since all of the development of CHIM-XPT has been done by only three people who share a dedication to a minimalistic programming style, the program is fast, lean, compact, and efficient even though it has tremendous power and versatility.

-MHR//4 April 2012

CONTENTS

1. INTRODUCTION

CHIM is a FORTRAN computer program for computing multicomponent heterogeneous chemical equilibria among solids, gases, and an aqueous phase (Reed, 1982). By computing equilibria in a series, with small changes in composition (X), pressure (P), or temperature (T) between steps in the series, CHIM-XPT can model complex processes such as cooling of hydrothermal solutions, reaction of solutions with rock, fluid-fluid mixing, gas titrations, boiling, adiabatic decompression, condensation, and evaporation. Because the phase equilibria always include an aqueous phase, CHIM is specific to aqueous systems. For gas-solid-liquid systems, program GASWORKS (Reed and Symonds, 1993) can be used instead.

CHIM applies a Newton-Raphson numerical method to solve a system of mass-balance and mass-action equations, together with a heat balance equation if needed (Reed, 1982, 1998; Spycher and Reed, 1988). For a given temperature, pressure, and total composition of a chemical system, CHIM computes the compositions of the aqueous, solid, and gas phases at equilibrium. For a chemical system including a gas phase, enthalpy, instead of pressure, can be specified. The saturation pressure is then computed using a heat balance equation that takes account of temperature, enthalpy, and composition (Spycher and Reed, 1988; Reed, 1998). To model geochemical processes, CHIM provides for stepwise incremental changes in T, P, enthalpy or composition with re-calculation of the equilibrium phase assemblage, mineral compositions and aqueous composition after each step.

Although program CHIM was originally developed on CDC, IBM and VAX main frame computers, modern PC's run it quite well. For the past many years, we have been running CHIM at the command prompt under Windows. Other users run it on Macintosh machines. The size of the program source code is about 270 Kbytes; the executable code is about 530 Kbytes, so it runs easily under Windows; it is not yet a victim of GUI code-bloat. The output files sometimes add up to a rather large total, e.g. consuming 10 or 20 Mbytes of hard drive space for a single calculation series. Usually, one can afford to delete most of the output files, saving critical ones for reference, but relying mostly on the plot files and saved input files.

1.1 Testing Execution

Try out the demonstration files (CHIMRUN.dm*) that were distributed with the program. The easiest way to do this is to place all of the CHIM-related files in the same directory, then execute the program at the command prompt or in Windows Explorer. Take the following steps:

a. Place the following files in one directory: chim-xpt.exe, soltherm.xpt, minox.dat, CHIMRUN.dm*. If the soltherm file that you have is not named "soltherm.xpt", copy it to the name "soltherm.xpt". CHIM reads only "soltherm.xpt".

b. Copy (do not rename) one of the CHIMRUN.dm* files to the name "CHIMRUN.DAT". If you rename instead of copying, the file will be lost when CHIM overwrites it with an updated "CHIMRUN.DAT".

c. Type "CHIM", and watch it execute. Or double click the exe file in Windows Explorer.

d. Use a text editor (e.g. TextPad, Wordpad) to examine the output file, CHIMOUT.DAT.

e. If you wish to save the output file, copy it to another name, e.g. ch-dm1ou.dat. (see section 4.5, on use of batch files to save outputs).

f. Repeat steps b,c,d,e with the other demonstration files.

1.2 Component Species and Derived Species

In CHIM, the composition of the chemical system is defined in terms component species such as H^+ H_2O Cl^- Na^+ HS^- SO_4^{2-} HCO_3^- etc. Other species are expressed in terms of these component species (e.g. HCl NaCl H_2S H_2CO_3 HSO_4^-) and are referred to as derived species (Reed, 1982, 1998). Mineral and gas compositions are also expressed in terms of component species. The total chemical composition of the system is thus given as the total molar amount of component species (e.g. if HCO3- is the component species for carbonate, total HCO_3^- includes HCO_3^-, H_2CO_3, CO_3^{2-}, calcite, CO_2 gas, etc.). If desired, the activity of hydrogen ion can be specified (as pH), and the total molar amount of that component is computed from the input of its activity. This procedure is used to compute pH at high temperatures (Reed and Spycher, 1984; Reed, 1998).

1.3 CHIM Function

The equilibrium assemblage in the aqueous-solid-gas system at a given temperature, pressure, and total composition is determined by first computing the activities of all aqueous species. Generally, but not necessarily, the beginning of a calculation includes only an aqueous phase. After a first apparent equilibration, CHIM determines which solids should saturate (calculated saturation indices equal to or greater than 0), which solids are not saturated, and whether the solution boils (calculated gas saturation pressure of the solution exceeds the specified total pressure). If any phases become super- or undersaturated, CHIM recomputes chemical equilibrium including the supersaturated phases, or excluding the undersaturated phases. This process is repeated until all phases are correctly assigned to the saturated assemblage, and until no new phases are supersaturated. When this condition is reached, the calculated assemblage is truly equilibrated, having reached the minimum Gibbs Free Energy for the composition, and CHIM proceeds to the next step, which, depending on the particular model calculation, is either: 1) a temperature increment at constant pressure (cooling, heating, isobaric boiling or condensation); 2) a pressure increment at constant temperature (isothermal boiling or condensing); 3) an enthalpy increment at constant temperature (boiling or condensation); 4) a temperature increment at a pressure depending on a given, not necessarily constant, enthalpy, or a given T-P curve (boiling or condensation); 5) an incremental change in the total composition of the system (mixing of solutions, water-rock titration, evaporation), which can also result in varying temperature if two solutions of different temperatures are mixed. After each step, solids and gases can either be fractionated from the system, or retained as part of the total system, thus allowing modeling of either open or closed systems.

2. INPUT AND OUTPUT FILES

CHIM reads input files and writes output files. Input files include one for describing the specific geochemical system being modeled (CHIMRUN.DAT) and two files containing thermodynamic and stoichiometric data for aqueous species, minerals and gases (soltherm.xpt, minox.dat). The two principal output files are one that tabulates all calculation results in human-readable form (CHIMOUT.DAT) and one for plotting of results *via* program MINTAB. Additional output files are re-written input files for use in continuing the calculations (CHIMRUN.*).

The following list contains a brief description of the files read and created by CHIM. The I/O device variables and their currently assigned values that are shown in brackets at the end of each description are further discussed below.

CHIMRUN.DAT. Input data specific to each run. Contains title, input parameters, system bulk composition, molalities, activity coefficients, and other parameters. CHIMRUN can be created by program GEOCAL. CHIMRUN is automatically rewritten after each completed equilibration, and will therefore always contain data for the last successfully accomplished calculation step. This allows the modelling run to be interrupted at any point during execution and restarted as a pickup run. If one wishes to keep a copy of any given intermediate CHIMRUN file (which, by the way, we recommend), one must copy it to another file (e.g. "CHIMRUN at T182 C.DAT", for a temperature change run starting at 182°C) before rerunning CHIM. Such saved run files are often useful for repeating a calculation with variations or for a departure to a different type of process.
[variable: INP1; value: 4; file name: CHIMRUN]

SOLTHERM.XPT Thermodynamic data base for aqueous species, gases and minerals. Stoichiometry, log K(T), activity and fugacity coefficient data.
[variable: INP2; value: 1; file name: SOLTHERM.XPT]

MINOX.DAT Stoichiometry and molecular weight of chemical components (oxides, minerals, gases etc.) to be used as reactants in titration reactions such as water-rock reactions.
[variable: INP4; value: 3; file name: MINOX.DAT]

CHIMRUN.SAV. Output file for the pickup run. Contains the current CHIMRUN.DAT (INP1) data at the last apparent equilibration step (not the last successfully fully equilibrated step). This file can be used as an input file (CHIMRUN.DAT) to restart an aborted run.
[variable: IOUT3; value: 8; file name: CHIMRUN.SAV]

CHIMRUN.SA2. Output file for the pickup run after bomb. Contains the current CHIMRUN.DAT data used to start the last attempted equilibration step in a case where the step failed to converge, having reached the loop limit. This file can be used as input (CHIMRUN.DAT) to restart a bombed run in a case where the cause of the bomb is something that can be treated in the input file (e.g. solid solution undersaturation).
[variable: IOUT4; value: 9; file name: CHIMRUN.SA2]

CHIMOUT.DAT Main calculation results.
[variable: IOUT1; value: 10; file name: CHIMOUT.DAT]

CHIMPLOT.DAT Condensed calculation results for plotting purposes. This file must be saved each time the calculations are interrupted. Concatonated CHIMPLOT files serve as as input for plotting program MINTAB.
[variable: IPUN; value: 2; file name: CHIMPLOT]

Output to the computer screen is executed using Fortran "print" statements without a device assignment. Screen output is used for interactive assessment of the calculations, including responding to charge imbalance at startup, and posting temperature, pressure, pH, and the solid and gas phase composition after each equilibration. Step increments are also indicated. Most computers run so fast now that these data cannot be read during execution.
[formerly IOUT2]

The I/O disk file numbers that CHIM assigs to the I/O variables (INP1, INP2, ..., IOUT1...) enhance compatibility with various computer systems so that current I/O device numbers in the READ and WRITE statements in CHIM can easily be redefined if necessary. In the current version of CHIM, there are FORTRAN "OPEN" statements that assign certain explicit file names (in Windows-compatible syntax) to the various device name variables used in the READ and WRITE statements. This form of assignment is compatible with most Fortran compilers, but some users may choose to remove (or "comment-out") the OPEN statements and assign the files to device numbers in a "COM" or "EXEC" file. If one chooses to disable the OPEN statements in CHIM, it is necessary to assign each disk file to the corresponding device numbers prior to running the program.

3. FORMAT AND CONTENT OF INPUT AND OUPUT FILES

Reading input files, computing, then writing output files is what CHIM-XPT does. Good input makes good output, so it is worth while to take care in getting the input correct. Details of key user input file and the main output file are the main focus here; details for other files are given in the appendix. Although Fortran format descriptions are included below, we do not assume that users are familiar with FORTRAN formatting conventions. We assume that users will use a Windows (or Mac) text editor to write the CHIMRUN.DAT input file, starting with a template such as the CHIMRUN demonstration files (CHIMRUN.dm*) shown below and provided with the programs. Templates show the variable names and the limits of the spaces where input numbers must fit.

Suitable text editors are ones that save files in simple ASCII format and that provide a non-proportional font for display, thereby allowing one to position numbers in the correct spaces in the input file. The best text editor for WINDOWS use is TEXTPAD (shareware), although *Windows Notepad* works fine, but *not* Wordpad. Word processors (e.g. Word Perfect, MS Word) can be used, but they are a pain in the neck for this purpose and should be avoided.

For each record (line) in the files described below, formats are given in parentheses in standard FORTRAN notation. Essential information about Fortran formats follows:

a) Integer variables must not include a decimal point, and there must exist at least one blank space or comma between each variable. For example, record 15, below, contains 18 integers. It is helpful, but not essential, to align each integer immediately below its descriptor in the line above. Record 15 MUST contain 18 integers, i.e. no blanks may be used to represent zeros.
b) Real variables (E, F and G formats, e.g. E10.4, F10.5, G15.9) must have decimal points (normally, don't worry about exceptions) and may begin and end anywhere within their field.
c) Any field labeled as "E" accepts a simple real number (e.g. 3.52) without the "E" notation (e.g. 3.52e-0).
d) Real run parameters in records 5, 8 and 11 are “free-format” meaning that they are properly read as long as there is at least one blank space or comma between each real value. It is helpful to align each real value immediately below its descriptor in the line above. The “free format” requires that records 5, 8 and 11 MUST contain 8, 3 and 8 real values, respectively (no blanks).
e) Beginning at record line 18, real numbers are input with a normal format, meaning they may begin and end anywhere within their field, but they need be within their field; a comma or blank does not serve to separate numbers. For example, record 18, below (I5, 13X,4(G19.13)), contains four real numbers (preceded by an integer), each of which is allowed nineteen spaces within which the number must fit. The number entries do not need to contain any particular number of decimal places, despite the "-.13" form in the formats.

3.1 The run file CHIMRUN.DAT (INP1, IOUT3, IOUT4)

The CHIMRUN.DAT file contains the data specific to each modelling run. For most users, this file is the only one that has to be created or modified prior to running CHIM. Program GEOCAL can be used to create the original version of this file (see further mention of GEOCAL in chapter 4) or an existing CHIMRUN file from an earlier run or one of the CHIMRUN.dm* demonstration files may be used.

After each successful complete equilibration, CHIM rewrites the CHIMRUN file in CHIMRUN.DAT (INP1); after partial equlibrations, CHIM rewrites a CHIMRUN.sav file; and after each loop-limit bomb, it writes a CHIMRUN.sa2 file (see chapter 4 for more on use of these files). In each case, the rewritten files contain all variable names and field delimiters with correct formats and all data appropriate to the last calcuation step, thereby providing the information needed to restart a run. In this chapter, the formats of each record, and the definition of each variable in the CHIMRUN file are given. To understand and set up the run characteristics of this file, refer to chapters 4 and 5. Example CHIMRUN files are given at the end of this section.

A description of CHIMRUN file content and formats follows. The "record" numbers shown below are simply line numbers in the file, and can be determined by counting down from the top. (For most of the input parameters, the variable names shown by labels in the run file are the same or nearly the same as the Fortran program names for those variables. Where they differ significantly, the Fortran names are given in parentheses in the following explanation of input.)

Example CHIMRUN.DAT file

```
1    Test file for CHIM-XPT. Mixing of cold water into metal bearing water starting at 199.97 C.
2    Illustrates fluid-fluid mixing. CHIMRUN demo-3
3
4    <  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><  volbox-1  ><rhofresh>< rhoroc >
5     .1000E-11    .00000 500.00000 199.97     25.00000      .00000      .00000    .00000
6
7    < step increm >< step limit  >< total mixer >
8     .5000000E-01   .5             .000000000
9
10   <  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
11       .00000    .00000    .00000  90.0000  .0000E-00    .0000 1082.4053  .1000E-10
12
13   l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
14   hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
15       1    3    0    1   70    2    2    0    0    0    0    1    0    0    0    0    0    0
16
17    saq> <   name   >   total moles   >< trial molality  ><       gamma     ><mixer total moles>
18       1 H+             .323435162E+00     .430247534E-05          .4449        .00000000E+00
.        2 H2O            .996569951E+00     .100000000E+01          .9517        .10000000E+01
.        3 Cl-            .154540006E+01     .116999249E+01          .4691        .00000000E+00
.        4 SO4--          .188639263E-03     .810540312E-04          .0440        .00000000E+00
         5 HCO3-          .349928002E+00     .206444637E-01          .4929        .00000000E+00
         6 HS-            .140303105E-04     .297172490E-05          .4717        .00000000E+00
         7 SiO2(aq)       .281174095E-02     .277938411E-02         1.0000        .00000000E+00
         . . . lines omitted here
        19 Au+            .311096068E-11     .626141090E-20          .5031        .00000000E+00
        22 Ba++           .406440000E-05     .110589176E-05          .0446        .00000000E+00
        23 F-             .163040000E-02     .125756610E-02          .4232        .00000000E+00
        25 H3AsO3         .129640000E-03     .129144357E-03         1.0000        .00000000E+00

     <     minerals     >  < min trial moles>

     <    reactants     >  < weight percent ><  ppm? >

     < mins to suppress >
     fmq_HS-1
     sulfur_gas
     Fe-staurolite
     kf-ab-equil

     < don't fractionate>

     <  T-P curve data  >
```

* Records 1 and 2 (10A8; write text): TITLE, two 80 character lines. Use this space to record input data sources AND a few notes on what this particular run does that distinguishes it from other runs. Title notes become your primary record of what you are doing in making this run.

* Records 3 and 4: skipped by CHIM on input. When the CHIMRUN file is written by CHIM or GEOCAL, these programs output records such as 3, which is blank, and 4, which contains format indicators for the next record.

* Record 5. Real variables (free format: space or comma separates numbers): ERPC, PH, PFLUID, TEMP, TEMPC, VOLBOX-1, RHOFRESH, RHOROCK,

ERPC: Convergence limit on mass-balance and mass-action equations (default value is 1.e-12). When all equations are solved within ERPC precision, the program assumes convergence. When setting ERPC, keep in mind that most computer systems have 16 significant digits in double precision, and CHIM might fail to converge if ERPC is smaller than 10-14 Convergence will definitely fail if ERPC is smaller than 10-16.

PH: pH of the solution; regardless of the actual solution pH, the variable "PH" is nearly always set to zero, for reasons explained below. If the variable PH is non-zero, the total molar amount of H+ ion in solution will be computed; also, a non-zero value of PH will cause pH to remain fixed at the specified value during the run. If PH is zero, the pH will be calculated from the given total amount of H+. The initial total amount of H+ ion is usually drawn from an earlier run with program SOLVEQ-XPT. Think about how you use the pH setting. As mentioned above, it is nearly always set to zero (blank) because it is rare that we wish arbitrarily to constrain pH to a constant value. Be sure to input a valid TOTAL MOLES(H+) if you are not setting pH.

PFLUID: Initial pressure of the system, in bars. Check SOLTHERM data file for the current pressure limits of thermodynamic data if one is modelling systems at elevated pressures.

TEMP: Initial temperature of the system, in degrees C. Check SOLTHERM data file for the current temperature limits of thermodynamic data if modelling at temperatures above 25 °C. Temperature is currently limited to the 0.01-600 °C range.

TEMPC: Temperature of the mixing solution, in deg.C, for fluid-fluid mixing calculations ("coolbrew" option). If TEMPC is non-zero, this parameter turns on the "coolbrew" option (see chapter 5). This option (TEMPC non-zero) must not be used with the MINSOLV or INCRP options below. TEMPC non-zero disables the MINSOLV option, but is overridden by the INCRP option.

VOLBOX-1 (Fortran name: VBOX1): Volume of box-1 in cubic centimeters.

a) Box-1 calculation: Set volbox-1 to the volume of the rock plus the volume of pore space in box-1.

b) Porosity calculation in a minsolv run (rock titration, minsolv=1). There are two ways to regard porosity. These two, and corresponding settings of volbox-1 are as follows:

i. Porosity refers to porosity of the altered rock, i.e. porosity within the confines of the bounding surface of the originally unaltered rock. Set initial volbox-1 to zero; CHIM will increase it as rock is titrated. Porosity results are then a comparison of the reactant rock volume to the volume of the minerals replacing it.

ii. Porosity refers to the porosity of the total system: rock plus water. Set initial volbox-1 to the volume of an imaginary vessel containing the water into which the first bit of rock is titrated

(e.g. 1000 cm^3 for a 1 kg of starting solution with density 1.0).

As one may detect, the use of box-1 is complicated. See notes in Chapter 4 on computing porosity and box-1 (flush) calculations. The value of vbox1 may be set to a bogus number without materially affecting chemical results, but do not believe output pertaining to porosity unless vbox1 is properly set.

RHOFRESH: Density (g/cm^3) of the fresh input fluid for box1, used in flush calculations. The fluid composition is input from MIXER TOTAL MOLES. See Chapter 4 for details.

RHOROCK: Density of reactant rock in a minsolv-type calculation (minsolv = 1). Used to calculate porosity.

* Records 6 and 7: skipped by CHIM on input, as for records 3,4.

* Record 8. Real variables (free format: space or comma separates numbers): STEP INCREM, STEP LIMIT, TOTAL MIXER

STEP INCREM (Fortran name: SINC): Increment size for calculation steps, such as grams of rock or degrees of temperature change. STEP INCREM has different meanings, depending on the type of calculation, as specified in settings of other parameters:

a) The default meaning is a temperature increment in degrees C. Set it negative for cooling, and positive for heating. Other meanings (not temperature) depend on settings outlined below.
b) For titrations of rock, gas, or water into an aqueous phase (by setting MINSOLV, below, to a non-zero value), STEP INCREM is the reactant titration increment in grams or moles.
c) For a non-zero value of the INCRP parameter, described below, STEP INCREM refers to a pressure increment in bars, or an enthalpy increment in kilocalories.
d) For fluid-fluid mixing, indicated by setting TEMPC, below, to a non-zero value, STEP INCREM is a unitless fractional titration factor (see chapter 5).

STEP INCREM cannot be zero. If set to zero, it is defaulted to -5 for temperature change, or to 0.1 if mixing options are selected. If you do not want incremental calculations, set STEP LIMIT smaller than the current temperature, pressure, enthalpy or total mixing fraction value, thereby providing for a single equilibration.

STEP LIMIT (Fortran name: SLIM): Temperature, pressure, enthalpy, or total mixing fraction limit at which the execution of CHIM will stop. Which variable STEP LIMIT counts depends on the type of calculation. STEP LIMIT is used relative to the sign of the increment parameter STEP INCREM. If STEP INCREM is negative, STEP LIMIT is a lower limit, if STEP INCREM is positive, STEP LIMIT is an upper limit. For example, if the system is being heated, STEP LIMIT must be greater than TEMP for the calculations to proceed. If if it is being cooled, then STEP LIMIT must be less than TEMP. In either case CHIM will stop once TEMP reaches STEP LIMIT. Similarly, when modelling fluid-fluid mixing or water/rock/gas titrations, CHIM stops once TOTAL MIXER, below, reaches STEP LIMIT.

TOTAL MIXER (Fortran name: TOTMIX): Total current amount of titrated stuff (mixer). In fluid-fluid mixing or titrations of rock, gas or water, TOTAL MIXER is a summation of all increments in the run since the beginning; e.g. for titrating albite by weight, TOTAL MIXER is

the total number of grams of albite titrated to this point. The particular controls are as follows:

a) For fluid-fluid mixing (TEMPC non-zero), TOTAL MIXER is the current total fraction of mixing solution already added to the original solution, where "fraction" refers to whatever is listed in the "mixer total moles" column (see below).
b) For titrations of rock, gas or water (MINSOLV below non-zero), TOTAL MIXER is the total amount of reactant already added to the original solution, in grams or moles depending on the value of MINSOLV below.

At the start of a fluid-fluid mixing or rock titration calculation, set TOTAL MIXER to zero. Thereafter, TOTAL MIXER is the sum of all previous mixing increments (STEP INCREM), and is computed by CHIM and inserted in the pickup CHIMRUN files. The user never changes TOTAL MIXER, except to set it to zero at the very beginning.

* Records 9 and 10: skipped by CHIM on input, as for records 3 and 4.

* Record 11. Real variables (4F10.5,E10.4): ENTH, SENTH, DENTH, TOTWAT, SOLMIN, RM, AQGRM, SUPRNT

ENTH: Current total enthalpy of the system (aqueous + gas) in Kcal, for boiling calculation with enthalpy constraint. (ENTH = "enthalpy"). If not specified, the default value is calculated by CHIM as the enthalpy of the aqueous phase at the current temperature and pressure (see chapter 5). Ignore for calculations other than boiling.

SENTH: Total enthalpy of the system at the start of a boiling calculation, in Kcal. (SENTH = "starting enthalpy"). The default value is equal to ENTH. Ignore for calculations other than boiling.

DENTH: Optional enthalpy gain or loss for the system, in Kcal per °C, for boiling calculations with enthalpy constraint. (DENTH = "delta enthalpy"). From one step to the next, the current total enthalpy changes from ENTH to ENTH + TINC x DENTH (where TINC is "temperature increment, set in "step increment", positive or negative). Thus, for cooling use a negative TINC and positive DENTH, use DENTH = zero for isoenthalpic boiling. and use a positive TINC with positive DENTH is for heat gain. Ignore for calculations other than boiling.

TOTWAT: Maximum weight percent of the total system (gas + liquid) allowed to boil (assuming mainly H_2O gas). The default value is 90 wt.%. This parameter is used to limit the trial amounts of H_2O in the gas phase when computing the equilibrium with a gas phase, to avoid convergence problems in rare cases. If more than TOTWAT percent of of the system boils, make sure to reset TOTWAT to a higher limit or convergence will fail. Ignore TOTWAT for calculations other than boiling, and ignore for most boiling calculations.

SOLMIN: Maximum negative molar amount of pure phases allowed to equilibrate (does not affect solid solutions or mixed gases). (SOLMIN = "solid minimum"). If pure solids or gases were previously saturated, but their current computed trial amounts become smaller than SOLMIN during computation of the saturated assemblage (during the Newton-Raphson iteration process), these phases are removed from the saturated assemblage. SOLMIN is active only after the 5th iteration, and only if set to a negative value. This option might be difficult for a novice to

use. If you are not familiar with the saturated mineral selection process in CHIM, set SOLMIN to any positive value to disable this option. Refer to chapter 4 for more details on how to use this parameter.

RM: Parameter between 0 and 1 to multiply mass balance and mass action equations to help convergence in calculations that do not converge otherwise. This forces residuals to decrease during convergence. RM must be set to zero unless there are convergence problems. Use only as last resort (see chapter 6), as RM non-zero might cause convergence to fail in a system that would normally converge with RM = 0.

AQGRM: Total amount in grams of aqueous phase at the start of a rock titration calculation. (AQGRM = "aqueous grams"). AQGRM is used only if the MINSOLV option for rock titration is enabled. Its only purpose is to compute the weight ratio of starting water to added reactant (e.g. water/rock ratio), equal to AQGRM/TOTAL MIXER. AQGRM never changes in the course of a modelling run. If input as zero, it is defaulted to the weight of the aqueous solution for the current run. Thus, if you're setting up a starting CHIMRUN for a rock titration, it is easiest to set AQGRM to zero and let CHIM compute it.

SUPRNT: Minimum molality of printed output derived species. (SUPRINT = "suppress print"). Any species with calculated molalities less than SUPRNT will not be printed on the output. SUPRNT helps reduce files sizes and avoid printing lenghty and useless output thereby pointlessly contributing to the further deforestation of the slopes of the Western Cascades. Default value is 10^{-10}.

* Records 12, 13 and14: skipped by CHIM on input, as for records 3 and 4.

* Record 15. Integer variables (16I5): L/V-HiP, CHGBAL, IFRAC, IPUNCH, NLOOP, ISTEP, LIMSOL, LOOC, IENTH, ITREF, IDEAL, IPSAT, INCREM, INCRP, MINSOLV, NEUT, AWATER, MINCHG.

L/V-HiP: Selector for T-P data: zero or one.
Zero (0) limits P-T to H_2O liquid-vapor saturation, T = 25-350 °C, P = 1-165.2 bar; P is computed by CHIM for T specified in CHIMRUN (PFLUID input is ignored).
One (1) allows T and P conditions specified in CHIMRUN to extend from 0.01-600°C and 1-5000 bar–the P-T space where water density exceeds 0.35 g/cm^3.

CHGBAL (Fortran name: C): Index number for component species ion to be used for charge balance if PH is given or if the starting solution is not in charge balance, whereupon the user is asked for permission to adjust charge. CHGBAL is the sequence position of the selected ion in the list of component species in SOLTHERM data file. In most cases, charge balance is set on chloride Cl^-, C = 3, and generally it is not actually changed because the solution is already in charge balance from a previous SOLVEQ-XPT run. CHGBAL (C) is further used to set the maximum allowable charge imbalance of the solution, which is 10^{-14} x C ion total molality. If charge imbalance exceeds this limit, execution stops (usually because of an error in the stoichiometry of a species or mineral, see chapter 6).

IFRAC: Selector for mineral and gas fractionation, 0, 1, 2, 3, 4 or 5. “Fractionation” refers to removal of saturated minerals or gases from the system after each equilibration.

Zero (0) results in no fractionation.

One (1) fractionates solids only.

Two (2) fractionates gases only.

Three (3) fractionates solids and gases. If the enthalpy constraint is enabled, gas fractionation also fractionates gas heat (Raleigh fractionation).

Four (4) engages the "DONTFRAC" option, whereby all minerals except those listed in DONTFRAC (see below) are to be fractionated from the system after each titration step.

Five (5) engages the Box-1 option (see below).

IPUNCH: Selector for plot file production. A *non-zero* value yields a condensed version of the calculation results written in a separate output file (device variable IPUN) for plotting purposes. (This parameter name is unchanged since the days of punching a plot file on cards.) See CHILPLOT file in this chapter.

NLOOP: The maximum allowed number of Newton-Raphson iterations in the convergence calculation. (NLOOP = "number of loops"). If CHIM has not converged after NLOOP iterations, non-convergence is assumed, and the execution is aborted. NLOOP = 70 is a good number. Most cases are solved after 10 to 20 iterations (loops). Generally, a case that is not solved after 70 iterations will not converge, however in some calculations where a redox boundary is being crossed, NLOOP as large as 150 is necessary. If NLOOP is set to zero, no calculations are performed. The execution is stopped after echoing all input data, all selected input parameters, and an indexed list of all aqueous species, gases and minerals selected from the data file SOLTHERM for the current calculation. NLOOP = 0 is useful for double checking all input parameters before starting a modelling run.

ISTEP: Selector for extra output, 0, 1 or 2.

Zero (0) setting yields normal output.

One (1) yields extra output for closer inspection of the calculation progress. Generally, *one* is only used for debugging purposes.

Two (2) yields additional detail (relative to a *zero* setting) on phase selection, but not as much as for a *one* setting; this is commonly of interest, especially to beginners and for untying numerical knots.

LIMSOL: Selector for treatment of solid solutions, 0,1, or 2.

A *non-zero* value enables inclusion of mineral solid solutions and mixed gases in the calculations. (LIMSOL = "limit of solid solutions").

Zero (0) causes solid solution end-members and gases to be treated as separate phases.

One (1) allows normal solid solution treatment, but undersaturation of solid solution endmembers is sometimes not detected, resulting in convergence failure. In which case, setting the parameter to

Two (2) allows solid solutions that become undersaturated to be automatically removed. However, rarely, a *two* setting results in the removal of solid solutions that should stay saturated (see chapter 4), leading to an infinite loop. Set LIMSOL to *one* unless you suspect that a saturated solid solution is becoming undersaturated.

LOOC: Determines the mineral selection method if more than one mineral becomes supersaturated in a given equilibration step. (LOOC = "COOL" spelled backward; there was a reason for this in the beginning, but it's a long story).

Zero (0) results in the selection of the most supersaturated mineral.

Non-zero results in back stepping, by successively setting SINC = -SINC/2, to the point where only one mineral supersaturates. LOOC = 0 generally saves computer time, output and trees (or disk space, these days). LOOC is reset to 0 if the back step becomes smaller than 0.05. Avoid setting LOOC non-zero at the start of a calculation because it is common at the start for there to be multiple supersaturated minerals.

IENTH: A *non zero* value turns the enthalpy balance constraint on. If the enthalpy of the system is not given (in ENTH space), the total enthalpy is calculated as the enthaply of the aqueous phase at the current temperature (TEMP). If IENTH is non-zero, but no gases are currently saturated, the enthalpy constraint is not enabled, but the enthalpy of the aqueous phase is calculated (see chapter 5).

ITREF: This parameter is used to activate iterative refinement when solving the system of non-linear equations. ITREF should always be set to zero (no iterative refinement), unless convergence problems arise. ITREF = 1 results in computing residuals, but not iterative refinement. In order to print these residuals, ISTEP must also be set to 1. ITREF = 2 results in minimizing the residuals by one or more iterative refinements, in order to help achieve convergence. This is a last resort option (see chapter 6).

IDEAL: Controls treatment of gas phase non-ideality.

Zero (0) results in treating gases as real and non-ideally mixing, for example in boiling runs.

One (1) causes ideal mixing of real gases.

Two (2) causes ideal mixing of ideal gases.

IPSAT: Controls saturation pressure calculation. A *non-zero* value produces a computation of the saturation pressure of the solution and composition of the gas phase at exact saturation. (IPSAT = I-"pressure of saturation" with gas phase). IPSAT is disabled if gases are already saturated. A *zero* setting results in no computing of the saturation pressure of the solution, and first boiling will occur only when the sum of the fugacities (and not partial pressures) reaches the value of PFLUID (see chapter 5).

INCREM: Provides for immediate step. A *non-zero* value produces an immediate step increment, without first equilibration of current step. Use to jump ahead in titration (or temperature change). If fractionation is selected (IFRAC non-zero), INCREM is reset to 0, and no immediate titration takes place. INCREM is used primarily to untie numerical knots, i.e. to jump start a run that diverges at the current equilibration.

INCRP: Controls pressure changes, 0, 1, or 2.

Zero (0) allows stepping in variables other than pressure.

One (1) increments pressure instead of temperature (as in isothermal boiling). STEP INCREM and STEP LIMIT must be pressure values in bars instead of temperature.

Two (2) increments enthalpy at constant temperature and turns IENTH on (the pressure is

therefore being solved for), and STEP INCREM and STEP LIMIT must be enthalpy values in Kcal. For INCRP = 2, TOTAL MIXER is the total enthalpy added to or removed from the system (sum of all previous STEP INCREM). In a closed system, TOTAL MIXER is therefore be equal to the current enthalpy of that system, ENTH.

A *non-zero* INCRP value always overrides non-zero MINSOLV or TEMPC values.

MINSOLV: Controls titration calculations, 0, 1, 2, 3, 4. A *non-zero* value enables the modelling of titrations of rock (usually, sometimes gas) into an aqueous phase. This option causes CHIM to read the data file MINOX (device INP4), which contains stoichiometries of reactant minerals, gases, oxides, or of any other reactant compounds (see chapter 5). Set MINSOLV as follows:

One (1) is for titration of all reactants in grams, therefore specifying STEP INCREM and STEP LIMIT in grams.

Two (2) has the same effect as *one,* except that only the reactants that are not already equilibrated with the aqueous phase are titrated. When using this option, the reactant name and specific spelling, as given in MINOX.DAT must match the corresponding mineral in SOLTHERM.XPT so that CHIM can recognize what equilibrated reactant not to titrate.

Three (3) provides for titration of all reactants in moles, therefore specifying STEP INCREM and STEP LIMIT in moles.

Four (4) is the equivalent of MINSOLV = 2, but for titration in moles.

If by mistake both TEMPC ("coolbrew" option) and MINSOLV are non-zero, MINSOLV will be reset to zero. Also, INCRP not zero overrides the MINSOLV option.

NEUT: Controls activity coefficients 0, 1, 2, 3. It was originally for controlling setting of gammas for neutral species, but is now also used to set gamma for all species to unity.

Zero (0) sets gammas for species flagged in SOLTHERM by azero = 9.99 to gamma(CO_2). Used for dissolved gases (CO_2, H_2S, etc.). Gammas for all other neutral species (SiO_2, AgCl, etc.) set to 1.0 (default).

One (1) sets gamma for all neutral species to 1.0.

Two (2) sets gamma for all neutral species to gamma(CO_2).

Three (3) sets gamma for all species to 1.0.

AWATR: Controls water activity, 0,1,2.

One (1) sets activity of H_2O = 1.0.

Not-one sets activity of H_2O using subroutine LIETZKE or BOWERS. NEUT = 3 overrides this option.

MINCHG: A special control for fake minerals, 0,1.

Zero (0): no function is executed.

One (1) allows use of charge imbalanced minerals in SOLTHERM and MINOX, and forces fluid charge balance at every step, to allow use of charged fake mineral buffers e.g. HX pH buffer.

* Records 16 and 17: skipped by CHIM on input, as for records records 3 and 4.

The number of the next records depends on how many component species are included in the

chemical system (one record per component species).

* Next records, one record per component species. Mixed values (I5,1X,A12, 2E19.13, 2G19.13): SAQ(i), NAME(i), TOTAL MOLES(i), TRIAL MOLALITY(i), GAMMA(i), MIXER TOTAL MOLES(i)

SAQ identifies species in the calculation. SAQ is an integer array that contains the identifying numbers of the component species that are needed for the present calculation. The identifying numbers are the sequence positions of the component species as listed near the top of the SOLTHERM data file. (SAQ = "SEQUENCE, AQUEOUS"). That is, the numbers match the order of component species listed in SOLTHERM (e.g. H^+ is 1, H_2O is 2, Cl^- is 3, SiO_2 is 7, O_2 is 31, etc..). SAQ, and not NAME, below, identifies which component species will used for the present calculation.

NAME contains the names of the selected components species identified by SAQ above. NAME here is a dummy variable which is skipped by CHIM on input; it is part of the record only to improve the clarity of the CHIMRUN file. Programs GEOCAL and CHIM automatically read the names of component species from SOLTHERM data file (as specified by the values of SAQ above), and writes these names in the NAME space above when rewriting CHIMRUN files.

TOTAL MOLES (Fortran name: MTOT) contains the total number of moles of component species, SAQ, in the system. For water, TOTAL MOLES must be in kilograms. TOTAL MOLES defines the total composition of the chemical system, including aqueous species, minerals and gases. TOTAL MOLES values are generally positive, but can also be zero or negative if the system contains phases or derived species that are expressed in terms of a negative amount of a component species (e.g. $NaOH = -1\ H^+ + 1\ Na^+ + 1\ H_2O$, therefore contains negative H^+; see discussion above and in Reed 1982, 1998). The sum of all TOTAL MOLES values must be in charge balance, within limits defined by the charge balance ion (see CHG BAL parameter in record 15).

TRIAL MOLALITY (Fortran name: MTRY) contains the trial molalities of component species SAQ. These are initial estimates of the molalities of each individual component species, which are what CHIM solves for (and which cannot be less than zero, in contrast to TOTAL MOLES values). The closer these initial trial values are to the actual (unknown) molalities, the better are the chances for CHIM to converge on a numerical solution. TRIAL MOLALITY values may be estimated (typically within four orders of magnitude), or computed with an earlier run of program SOLVEQ-XPT. For water, TRIAL MOLALITY is internally set to 1 kg, and any input value is ignored. After an initial equilibration step, correct TRIAL MOLALITY values (actual molalities of each species) are computed and automatically rewritten in this file (see chapter 4). Default TRIAL MOLALITY values are 10^{-10}.

GAMMA contains activity coefficients of component species SAQ. For an initial run, these must be estimated. Default GAMMA values are unity. After an initial calculation step, correct GAMMA values are computed and automatically rewritten in this file (see chapter 4).

MIXER TOTAL MOLES (Fortran name: COMTOT, for “cold mtot”) contains the total

moles of component species SAQ in the mixer solution. MIXER TOTAL MOLES for water must be in kilograms. MIXER TOTAL MOLES is generally used only if the fluid-fluid mixing option is selected (TEMPC in record 5 non-zero), and defines the total composition of the mixer solution (which may be any type of reactant that can be expressed in terms of the selected component species). As for TOTAL MOLES, MIXER TOTAL MOLES must be in charge balance.

* Next record: MUST BE BLANK to indicate end of component species data.

* Next record: skipped by CHIM on input. Similar to record 4.

The number of the subsequent records depends on how many minerals and gases are currently saturated in the system (one mineral or gas per record; if none, no records).

* Next records. Mixed values (A20, 2X, G18.12): MINERALS(i), MINERAL TRIAL MOLES(i)

MINERALS (Fortran name: SATMIN) contains the names of minerals and (or) gases currently saturated in the system. MINERALS must match exactly the spelling of phases in the SOLTHERM data file; if not CHIM will stop execution and let you know of the mismatch.

MINERAL TRIAL MOLES (Fortran name: MINTRY) contains the trial molar amount of mineral or gas, MINERALS. Just as for TRIAL MOLALITY above, initial MINERAL TRIAL MOLES values must be estimated, but the user rarely needs to do this. After an initial calculation step, correct MINERAL TRIAL MOLES values (the actual molar amount of each phase) are computed and are automatically rewritten in CHIMRUN (see chapter 4). Default MINERAL TRIAL MOLES values are 10^{-9}.

* Next record: MUST BE BLANK to indicate end of saturated phases list.

* Next record: skipped by CHIM on input. Similar to record 4.

The number of the following records depends on how many reactants are specified when modelling rock titrations (as defined by setting MINSOLV non-zero in record 15). There is one reactant per record, and no records if no reactants. If MINSOLV is non-zero, there must be at least one reactant. If MINSOLV is zero (no rock titration intended), an reactants listed are read properly, but are not used. This capability is convenient for complex calculations wherein one changes from rock titration to heating and back to rock titration, for example.

* Next records. Mixed values (A20, 2X, G18.12, A8): REACTANT(i), WEIGHT PERCENT(i), PPM

REACTANT (Fortran name: NOMOX, for “name of oxide”) contains the name of the reactants (oxides, minerals, gases, etc.) to be titrated. REACTANT must match exactly the spelling of reactants given in the MINOX data file; if not, CHIM stops execution and lets you know of the mismatch.

WEIGHT PERCENT (Fortran name: WTPC) contains the composition in weight or mole percent of reactants (these do not have to add up to one hundred). If MINSOLV (in record 15) is 1 or 2, WEIGHT PERCENT must be in weight percent; if MINSOLV is 3 or 4, WEIGHT PERCENT must be in mole percent.

PPM allows the user to specify any composition value given in the "weight percent" column in parts per million or parts per billion by writing "ppm" or "ppb" in the PPM space, taking care to write the "ppm" or "ppb" starting at the leftmost end of the input field (right under the "<" symbol) and using lower case (ppm not PPM).

* Next record: MUST BE BLANK to indicate end of reactant data.

* Next record: skipped by CHIM on input. Similar to record 4.

The number of the following records depends on how many aqueous species, minerals, and/or gases one is suppressing in the calculation (one name per record, and no records if no names). These records are optional, and are read until a blank line is encountered.

* Next record (A20): MINS TO SUPPRESS(i)

MINS TO SUPPRESS (Fortran name: SUPNAM) contains the names of aqueous species, gases or minerals that are suppressed in the calculations (one name per record). The names of these species must be spelled exactly like the corresponding species in SOLTHERM data file; if there is a mismatch, CHIM will **NOT** let you know, but you will know when you read the output file. Up to 50 names can be specified. Mineral suppression is commonly used to disallow kinetically disfavored minerals, selected on the judgement of the user.

* Next record: MUST BE BLANK to indicate end of suppressed items list.

* Next record: skipped by CHIM on input. Similar to record 4.

* Next Record: (A8) DON'T FRACTIONATE(i)

DON'T FRACTIONATE (Fortran name: DONTFRAC) contains the names of minerals (or fake minerals such as gas buffers like fCO2-3.5) that are not to be fractionated. The spelling of these minerals must match their spelling in SOLTHERM or else the program will not recognize them. Up to 19 minerals may be listed.

Be sure, if you use DON'T FRACTIONATE, to set IFRAC to 4 (above), indicating that all minerals except those listed in DON'T FRACTIONATE are to be fractionated from the system after each titration step. The DON'T FRACTIONATE option is useful for calculations for which the physical setting for the simulated system involves the flow of water through a rock matrix such that the aqueous phase separates from the minerals that precipitate from it, thereby leaving behind product minerals. Such minerals are "fractionated" from the chemical system. In some cases, one might wish to buffer the chemical system along the entire path with certain minerals or gas buffers (e.g. atmospheric) that are assumed to be present everywhere. In this case, we do not wish to fractionate the latter minerals, so they are listed in DON'T FRACTIONATE.

As currently programed, you cannot use DON'T FRACTIONATE in combination with fractionation of gases in a boiling calculation. You can use it if you are fractionating minerals during boiling but not if you wish to fractionate minerals plus gases.

* Next record: MUST BE BLANK to indicate end of items to not fractionate list.

* Next record: skipped by CHIM on input. Similar to record 4.

Next Record: T-P CURVE DATA(i)

T-P CURVE DATA(i) controls calculation path through P-T space, such as an adiabatic path. It contains up to up to 200 temperature-pressure points, expressed as T and P, in that order, one T-P pair per record. If this block contains one or more T-P points, CHIM will use these data to compute pressure for incremented temperature. For alternative other T-P variations to work (e.g. enthalpy constraint), or for constant pressure, this block MUST be empty. If not, the T-P curve data option will be applied and at any given temperature, CHIM will interpolate between the two nearest given T-P points of this file to compute pressure, overriding the value of PFLUID given in the CHIMRUN file. (Another, mostly obsolete, use of the T-P curve in boiling is addressed in Chapter 5.)

3.2 Example CHIMRUN Files

The following five files illustrate commonly used capabilities of CHIM. It is helpful to read over these files, referring first to the notes at the bottom of the files, then to the descriptions, above, of the variables and their potential settings. The same demonstration files are distributed with the program, thus they are available as templates to set up new run files. (In the following listing, the run files are offset by one space from the left margin relative to the proper files.)

CHIMRUN.dm1

```
Test file for CHIM-XPT.  Japanese Geothermal Water.  Cooling only.
See running notes, below.  CHIMRUN demo-1

<  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><volbox-1><rhofresh>< rhoroc >
0.100E-11    0.0000  500.0000  240.0000    0.0000    0.0          0.0      0.0

< step increm >< step limit  >< total mixer >
  -10.0000        100.00000       0.00000

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
   0.0000    0.0000    0.0000   90.0000 0.000E+00    0.0000 1049.7467 0.100E-19

l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
    1    3    0    1  470    2    1    0    0    0    0    1    0    0    0    0    0

 saq> <   name   ><   total moles   >< trial molality  ><       gamma     ><mixer total moles>
    1 H+           0.163232117E+00    0.374653884E-04    0.4737              0.0000E+00
    2 H2O          0.100000000E+01    0.100000000E+01    0.9813              0.0000E+00
    3 Cl-          0.663288390E+00    0.572164181E+00    0.3776              0.0000E+00
    4 SO4--       -0.147330528E-02    0.194107695E-09    0.0293              0.0000E+00
    5 HCO3-        0.139322102E+00    0.207583619E-03    0.4044              0.0000E+00
    6 HS-          0.274162218E-01    0.234429204E-03    0.3805              0.0000E+00
    7 SiO2(aq)     0.161905289E-01    0.637757237E-02    1.2135              0.0000E+00
    9 Ca++         0.299401172E-01    0.622041368E-02    0.0239              0.0000E+00
   10 Mg++         0.867510447E-03    0.260049195E-03    0.0186              0.0000E+00
   11 Fe++         0.260451779E-04    0.145185067E-08    0.0199              0.0000E+00
   12 K+           0.802097321E-01    0.731121296E-01    0.4141              0.0000E+00
   13 Na+          0.521970809E+00    0.467267486E+00    0.3824              0.0000E+00
   15 Zn++         0.500000000E-05    0.818590291E-10    0.0199              0.0000E+00
   16 Cu+          0.500000000E-06    0.386739006E-10    0.3814              0.0000E+00
   17 Pb++         0.200000000E-05    0.210274290E-08    0.0274              0.0000E+00

<     minerals     >  < min trial moles>
quartz               0.9812E-02

<    reactants     >  < weight percent ><  ppm? >

< mins to suppress >
fmq_HS-1
fCO2-3.5
kf-ab-equil

< don't fractionate>

<  T-P curve data  >
```

Running Notes

Graphite forms because a gas phase, which would contain CH_4, is not allowed.

File: CHIMRUN.dm1. Example CHIMRUN demonstration file illustrating a cooling of a geothermal water without boiling. Cooling, as opposed to other possibilities, is specified by a negative SINC in combination with zeros for TEMPC and MINSOLV. This run produces graphite as a mineral precipitate because the methane that boils out of the actual water is here constrained to go elsewhere.

CHIMRUN.dm2

```
Test file for CHIM-XPT.  Boil Broadlands Water
Water similar to Broadlands Well No. 2   CHIMRUN demo-2a

<  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><  volbox-1  ><rhofresh>< rhoroc >
 .1000E-11    .00000  82.8577  280.0000     .0000       .0000       .0000     .0000

< step increm >< step limit  >< total mixer >
-2.000000       100.000000     .000000000

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
    .00000    .00000    .00000  90.0000   .000E-00    .0000 1013.7045  .1000E-10

l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
    0    3    0    1  200    2    1    0    1    0    0    1    0    0    0    0    0    0

 saq> <   name   ><   total moles   >< trial molality  ><       gamma     ><mixer total moles>
    1 H+            .182217216E+00      .125063079E-05          .6904       .00000000E+00
    2 H2O           .100000006E+01      .100000000E+01          .9998       .00000000E+00
    3 Cl-           .307201670E-01      .284118035E-01          .6790       .00000000E+00
    4 SO4--        -.425769998E-02      .456842804E-09          .2520       .00000000E+00
    5 HCO3-         .183210000E+00      .187495855E-02          .6838       .00000000E+00
    6 HS-           .998581977E-02      .445512707E-03          .6795       .00000000E+00
    7 SiO2(aq)      .785534577E-02      .780506487E-02         1.0000       .00000000E+00
    8 Al+++         .225368011E-05      .159314158E-20          .0490       .00000000E+00
    9 Ca++          .356140000E-04      .120627182E-04          .2440       .00000000E+00
   10 Mg++          .235550282E-06      .512176025E-07          .2357       .00000000E+00
   11 Fe++          .801737198E-08      .204868143E-08          .2378       .00000000E+00
   12 K+            .371570000E-02      .359743827E-02          .6852       .00000000E+00
   13 Na+           .296330000E-01      .272827211E-01          .6793       .00000000E+00
   14 Mn++          .274042369E-08      .261293946E-10          .2393       .00000000E+00
   15 Zn++          .153000000E-07      .215599355E-14          .2378       .00000000E+00
   16 Cu+           .623740999E-07      .152138235E-11          .6791       .00000000E+00
   17 Pb++          .111000000E-07      .560483269E-12          .2491       .00000000E+00
   20 Hg++          .400000000E-08      .119110995E-30          .2467       .00000000E+00
   23 F-            .243910000E-03      .162298326E-03          .6698       .00000000E+00

<     minerals     >  < min trial moles>

<    reactants     >  < weight percent ><  ppm? >

< mins to suppress >
fmq_HS-1
fCO2-3.5
SO3,gas
S2,gas
kf-ab-equil
antigorite

< don't fractionate>

<  T-P curve data  >
```

Running Notes

a. Notice that P is set to 82.8577 bar, a small amount less than the saturation pressure for this fluid (82.8578), which was computed by a separate initial run in which boiling was not allowed.

b. To boil this system below 148 C, remove undersaturated chlorite solid solution by hand at 148, then continue. (Move clinochlore, daphnite and Mn-chlorite to the suppressed group).

OR

c. Reset limsol to 2 at 148, then run.

OR

d. Reset imcrem to 1, and delete clinochlore, daphnite and Mn-chlorite from the current minerals

list.

The problem at 146C is that chlorite solid solution is undersaturated, after having been saturated at higher temperature. You can verify that chlorite is dissolving by checking the moles of clinochlore at 150 and 152 degrees, where you will find much larger amounts that at 148C.

Option (b), above fixes the problem directly, by hand, by suppressing the chlorite.

Option (c) fixes the problem by invoking a mechanism in CHIM that detects a computed negative amount of solid solution end-member, then tosses the endmember from the system before it can be used to compute a negative mole fraction, which is mathematically confounding and disallowed. Option (b) cannot be set universally because it sometimes tosses endmembers (e.g. of gas phase) that belong, no matter what.

Option (d) fixes the problem by hand-removing the chlorite (but not supressing it, as in option (a)); setting increm to 1 causes chim-xpt to change T to 146C immediately upon execution, instead of first re-computing at 148C (where chlorite is still properly saturated); at 146C, chim finds that the system is now undersaturated in chlorite, so chim does not put it back in.

CHIMRUN.dm3

```
Test file for CHIM-XPT. Mixing of cold water into metal bearing water starting at 199.97 C.
Illustrates fluid-fluid mixing. CHIMRUN demo-3

<  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><volbox-1><rhofresh>< rhoroc >
 .1000E-11    .00000 500.00000 199.97     25.00000    .00000    .00000    .00000

< step increm >< step limit  >< total mixer >
 .5000000E-01   .5             .000000000

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
    .00000    .00000    .00000  90.0000  .1000E-10    .0000 1082.4053  .1000E-10

l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
    1    3    0    1   70    2    2    0    0    0    0    1    0    0    0    0    0    0

 saq> <   name   ><   total moles   >< trial molality  ><       gamma     ><mixer total moles>
    1 H+             .323435162E+00     .430247534E-05          .4449        .00000000E+00
    2 H2O            .996569951E+00     .100000000E+01          .9517        .10000000E+01
    3 Cl-            .154540006E+01     .116999249E+01          .4691        .00000000E+00
    4 SO4--          .188639263E-03     .810540312E-04          .0440        .00000000E+00
    5 HCO3-          .349928002E+00     .206444637E-01          .4929        .00000000E+00
    6 HS-            .140303105E-04     .297172490E-05          .4717        .00000000E+00
    7 SiO2(aq)       .281174095E-02     .277938411E-02         1.0000        .00000000E+00
    8 Al+++          .240727893E-05     .827265862E-15          .0011        .00000000E+00
    9 Ca++           .210522349E-02     .147256804E-02          .0372        .00000000E+00
   10 Mg++           .171772416E-03     .104663828E-03          .0305        .00000000E+00
   11 Fe++           .160330513E-05     .106995014E-05          .0321        .00000000E+00
   12 K+             .454561151E-01     .409605833E-01          .5001        .00000000E+00
   13 Na+            .152379835E+01     .114754512E+01          .4715        .00000000E+00
   14 Mn++           .344771227E-04     .253395534E-06          .0333        .00000000E+00
   15 Zn++           .746817628E-05     .445130487E-08          .0321        .00000000E+00
   16 Cu+            .170157126E-06     .606168018E-11          .4707        .00000000E+00
   17 Pb++           .156502066E-05     .155830882E-08          .0416        .00000000E+00
   18 Ag+            .427128103E-06     .132955923E-10          .4948        .00000000E+00
   19 Au+            .311096068E-11     .626141090E-20          .5031        .00000000E+00
   22 Ba++           .406440000E-05     .110589176E-05          .0446        .00000000E+00
   23 F-             .163040000E-02     .125756610E-02          .4232        .00000000E+00
   25 H3AsO3         .129640000E-03     .129144357E-03         1.0000        .00000000E+00

<     minerals     >  < min trial moles>

<    reactants     >  < weight percent ><  ppm? >

< mins to suppress >
fmq_HS-1
sulfur_gas
Fe-staurolite
kf-ab-equil

< don't fractionate>

<  T-P curve data  >
```

File: CHIMRUN.DM3. Example CHIMRUN file illustrating fluid-fluid mixing. In this case, a saline water (specified by TOTAL MOLES) at 200 °C (TEMP) is mixed with a 25 °C (TEMPC) pure water (specified by the 1.0 for H_2O in the MIXER TOTAL MOLES column). The MIXER TOTAL MOLES of H_2O of 1.0 means 1.0 kg of water. (If there were dissolved salts in the mixing water, they would be specified in moles using the rest of the MIXER TOTAL MOLES). The value of STEP INCREM (.05) indicates that .05 * 1.0 kilograms of water will be titrated on each step until a total of .5 (STEP LIMIT) increments have been added.

CHIMRUN.dm4

```
Test file for CHIM-XPT. Water-rock titration. Serpentinization at 25 °C of a simplified
harzburgite (no aluminum or trace elements) by meteoric water.  CHIMRUN demo-4.

<  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><volbox-1><rhofresh>< rhoroc >
 .1000E-11    .00000  10.00000  25.00000    .00000   1.00000    .00000   2.50000

< step increm >< step limit  >< total mixer >
     .001         .05             .0000

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
    .00000    .00000    .00000  90.00000 .0000E+00    .00000    .00000 .1000E-19

l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
    1    3    0    1  400    2    1    0    0    0    0    1    0    0    1    0    0    0

 saq> <   name   ><   total moles   >< trial molality  ><       gamma     ><mixer total moles>
    1 H+              .1304000E-04    .1000000E-06       1.0000             .0000E+00
    2 H2O             .9999882E+00    .1000000E+01       1.0000             .0000E+00
    3 Cl-          .1379741800E-03    .1000000E-03       1.0000             .0000E+00
    4 SO4--           .2550447E-04    .1000000E-06       1.0000             .0000E+00
    5 HCO3-           .1307000E-04    .1000000E-05       1.0000             .0000E+00
    6 HS-             .1000000E-15    .1000000E-16       1.0000
    7 SiO2(aq)        .1000000E-15    .1000000E-16       1.0000
    9 Ca++            .1447106E-04    .1000000E-06       1.0000             .0000E+00
   10 Mg++            .1000000E-15    .1000000E-16       1.0000
   11 Fe++            .1000000E-15    .1000000E-16       1.0000
   13 Na+             .1600710E-03    .1000000E-06       1.0000             .0000E+00

<     minerals     >  < min trial moles>

<    reactants     >  < weight percent ><  ppm? >
SiO2                    43.90
Fe2O3                    1.34
FeO                      6.49
MgO                     45.9
CaO                      0.60
Na2O                     0.0092
FeS                      .0685
NaCl                     0.0053

< mins to suppress >
fmq_HS-1
Fe-staurolite
antigorite
Al-free_chlorite
goethite
kf-ab-equil

< don't fractionate>

<  T-P curve data  >
```

File: CHIMRUN.DM4. Example CHIMRUN file illustrating water-rock titration.
Running Notes: High W/R (~1000g/0.05g) yields chrysotile, hematite and pyrite. After running, increase STEP INCREM, STEP LIMIT to 0.01, 0.5, and run again to get lower W/R, and chrysotile, brucite, magnetite, and pyrite. Increase again STEP INCREM, STEP LIMIT to 1.0, 100.0 to get chrysotile, brucite, magnetite, andradite, pyrrhotite, a H2-rich gas phase, and hyperalkaline fluid.

Other notes: Harzburgite (avg of 8) from Loney et al. J.Petr 12, 245-309 (1971). Meteoric water, coastal US, pH = 5.65; Berner & Berner (1987), in equilibrium with atmospheric CO2.

CHIMRUN.dm5

```
Test file for CHIM-XPT. Isoenthalpic cooling and depressurization of Butte, MT
magmatic fluid, using T-P curve option. CHIMRUN demo-5

<  erpc  ><   pH   >< pfluid ><  temp  ><  tempc ><volbox-1><rhofresh>< rhoroc >
 0.100E-11    0.0000 2500.0000  600.0000    0.0000  0.0         0.0000    2.5000

< step increm >< step limit  >< total mixer >
   -1.00           535.           0.0

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
    0.0000    0.0000    0.0000   90.0000 0.100E-08    0.0000 1200.0089 0.100E-10

l/v:0  chg    i    i    n    i  lim         i   it    i    i   in incr  min         a  min
hiP:1  bal frac punc loop step  sol looc enth  ref deal psat crem    P solv neut watr  chg
    1    3    0    1  500    2    1    0    0    0    0    0    0    0    0    0    0

 saq> <   name   ><   total moles   >< trial molality  ><       gamma     ><mixer total moles>
    1 H+            4.26236218407     0.294890462090E-02 0.498181303394E-02  0.00000000000
    2 H2O         0.936163170129       1.00000000000      1.00241697541      0.00000000000
    3 Cl-         0.651370661327     0.330677771807-233 0.761829597249E-01  0.00000000000
    4 SO4--       0.251722780732       6.20911466602    0.774854376215E-08  0.00000000000
    5 HCO3-        2.65611300000     0.356418351287-237 0.203048612556      0.00000000000
    6 HS-          1.16014414421     0.424089892359E-03 0.854515591635E-01  0.00000000000
    7 SiO2(aq)    0.143594323086     0.145203806002       1.00000000000      0.00000000000
    8 Al+++       0.694539525171E-03  1.17426571275     0.426332394531E-20  0.00000000000
    9 Ca++        0.527909890870E-03  8.85358206171     0.130045474355E-08  0.00000000000
   10 Mg++        0.206766517541E-04 0.494348438423     0.123601189451E-09  0.00000000000
   11 Fe++        0.876675378121E-02  8.63396374581     0.229942702424E-09  0.00000000000
   12 K+          0.125410131090     0.183099084138     0.312882648427      0.00000000000
   13 Na+         0.554599348266       1.97811443999    0.106124764209      0.00000000000
   14 Mn++        0.114950000000E-02  5.16377367197     0.358113923301E-09  0.00000000000
   15 Zn++        0.229933468376E-02 0.123856873183-235 0.229942702424E-09  0.00000000000
   16 Cu+         0.399609714897E-03 0.747819456972E-06 0.102426156741      0.00000000000
   17 Pb++        0.340172647310E-03 0.182237288550-236 0.455771947640E-08  0.00000000000
   18 Ag+         0.870084200000E-05 0.175807029399E-14 0.260209432613      0.00000000000

<     minerals     >  < min trial moles>

<    reactants     >  < weight percent ><  ppm? >

< mins to suppress >
SO2,gas
S2,gas
silica-amorphous
tridymite
antigorite
osumilite(1)
cordierite
H-cordierite
kf-ab-equil
spessartine
pyroxmangite

< don't fractionate>

<  T-P curve data  >
535.0   795.0
536.0   803.0
537.0   812.0
538.0   820.0
539.0   829.0
540.0   838.0
541.0   848.0
542.0   858.0
543.0   868.0
544.0   879.0
545.0   890.0
546.0   901.0
547.0   912.0
548.0   923.0
549.0   934.0
```

550.0	945.0
551.0	956.0
552.0	967.0
553.0	978.0
554.0	989.0
555.0	1000.0
556.0	1012.0
557.0	1024.0
558.0	1037.0
559.0	1050.0
560.0	1063.0
561.0	1077.0
562.0	1091.0
563.0	1107.0
564.0	1123.0
565.0	1139.0
566.0	1155.0
567.0	1171.0
568.0	1187.0
569.0	1203.0
570.0	1220.0
571.0	1238.0
572.0	1258.0
573.0	1280.0
574.0	1302.0
575.0	1325.0
576.0	1348.0
577.0	1372.0
578.0	1396.0
579.0	1421.0
580.0	1447.0
581.0	1473.0
582.0	1500.0
583.0	1528.0
584.0	1558.0
585.0	1589.0
586.0	1621.0
587.0	1655.0
588.0	1691.0
589.0	1729.0
590.0	1769.0
591.0	1811.0
592.0	1856.0
593.0	1903.0
594.0	1950.0
595.0	2000.0
596.0	2060.0
597.0	2140.0
598.0	2245.0
599.0	2365.0
600.0	2500.0

Running notes:

To proceed below 548 °C, remove undersaturated biotite solid solution by hand at 548, then continue. (Move annite and phlogopite to the suppressed group).

Other notes:

Isoenthalpic curve data is interpolated from data computed with SUPCRT92, Johnson J. W., et al. Computers and Geosciences. 7, 899-947 (1992).

3.3 The thermodynamic data file SOLTHERM.XPT (INP2)

The SOLTHERM data file contains all thermodynamic data for aqueous, gas, and mineral species. This file generally does not have to be modified by the user (but we do hope you add to it). The file is divided into seven parts as follows, beginning at the top: Comment area, Activity coefficients data (also including some miscellaneous data), Component species data, Derived species data (aqueous), Gas data, Mineral data, and Optional miscellaneous data. The content and format of this file are described in appendix A.

3.4 The reactant data file MINOX (IOUT 6)

The reactant file, MINOX.DAT is only read if the MINSOLV option for rock titrations is enabled (MINSOLV non-zero in CHIMRUN data file). This file contains data for an unlimited number of reactants that are to be used in modelling water/rock/gas interactions. Reactants are generally specified as oxides or minerals, but any other form of reactant may be entered in this file. The file is read until all reactants names (NOMOX) given in the CHIMRUN file are matched, or up to a blank line or end of file. The MINOX data file has a comment area at the top of the file, which MUST be followed by a line of stars to indicate the end of this area (at least 8 stars starting in column 1 will do).

Records following the line of stars are as follows, each record (A20, A1, 1X, F7.2, I2, 1X, 11(F6.3,I2)): NOMOX, XMW, ITOT, COEFM(i) and SPECM(i) i = 1 to ITOT

The format of these records is similar to the stoichiometry records of minerals and gases in the data file SOLTHERM (see appendix A) that records may be copied from SOLTHERM to MINOX with minor modification if desired. The user may choose to add reactants to this file that are not in the copy supplied on the distribution diskette. Some such records copied from SOLTHERM, contain additional data that are skipped upon input, and are not discussed here.

NOMOX is the name of the reactant. XMW is the molecular weight of the reactant. ITOT is the number of component species in the stoichiometry of the reactant. COEFM(i) contains the stoichiometric coefficient for species SPECM(i) in the reactant. SPECM(i) identifies the component species in the stoichiometry of the reactant, and corresponds to the sequence position of that species in the list of component species in the SOLTHERM data file (e.g. SPECM = 1 for H+, 7 for SiO2, etc.).

3.5 The main output file (IOUT 6)

The output file, CHIMOUT.DAT may become quite large, and we strongly recommend using the "pickup" method described in chapter 4 to generate manageable files when carrying out large calculations. Notice that the ISTEP = 1 option (see CHIMRUN file) makes the CHIMOUT.DAT file even larger.

Preceding the calculation results, CHIMOUT contains an echo of all of the run-specific data read by CHIM. Then calculation results are given, for each equilibration, divided into five parts: title block, speciation results, component distribution among phases, saturated gases and minerals, and mineral saturation indexes.

Example file: CHIMOUT.DAT

```
 ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
 Test file for CHIM-XPT. Mixing of cold water into metal bearing water starting at 199.97 C.
 Illustrates fluid-fluid mixing. CHIMRUN demo-3
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

  Number of loops used =    6   Loop limit =   70

  Temperature = 178.25 C   Pressure =  500.00 bar   Mixer fraction =     0.1500000

  Water: Moles liquid = 0.6397E+02   kg liquid  = 0.1152E+01
         Moles total  = 0.6364E+02   kg total   = 0.1147E+01  Activity = 0.9568
  Stoichiometric ionic strength = .1516000E+01   Osmotic coef. =  0.9140
  True ionic strength = .1123349E+01
  Chg. balance for total moles = -.1296E-03   Max. difference allowed = 0.1545E-03

                                  Log                  Log                  Log
   Species(n)       Molality   Molality    Activity   Activity    Gamma      Gamma

   1 H+           0.64023E-05   -5.1937 0.32555E-05   -5.4874 0.50848E+00   -0.2937
   2 H2O                                0.95679E+00   -0.0192 0.95679E+00   -0.0192
   3 Cl-          0.10975E+01    0.0404 0.58690E+00   -0.2314 0.53478E+00   -0.2718
   4 SO4--        0.14816E-03   -3.8293 0.80091E-05   -5.0964 0.54058E-01   -1.2671
   5 HCO3-        0.22976E-01   -1.6387 0.12683E-01   -1.8968 0.55202E+00   -0.2580
  -- species omitted here --
  17 Pb++         0.37610E-08   -8.4247 0.19073E-09   -9.7196 0.50711E-01   -1.2949
  18 Ag+          0.13081E-10  -10.8833 0.72217E-11  -11.1414 0.55206E+00   -0.2580
  19 Au+          0.37299E-21  -21.4283 0.20825E-21  -21.6814 0.55833E+00   -0.2531
  20 Ba++         0.15669E-05   -5.8050 0.82179E-07   -7.0852 0.52448E-01   -1.2803
  21 F-           0.11706E-02   -2.9316 0.58980E-03   -3.2293 0.50386E+00   -0.2977
  22 H2AsO3-      0.11771E-05   -5.9292 0.80198E-06   -6.0958 0.68134E+00   -0.1666
  26 AgCl,aq      0.23323E-08   -8.6322 0.23323E-08   -8.6322 0.10000E+01    0.0000
  27 AgCl2-       0.10448E-06   -6.9810 0.55872E-07   -7.2528 0.53478E+00   -0.2718
  28 AgCl3-2      0.67428E-07   -7.1712 0.35187E-08   -8.4536 0.52185E-01   -1.2825
  29 AgCl4-3      0.10465E-07   -7.9803 0.11745E-10  -10.9301 0.11223E-02   -2.9499
  33 Ag(HS),aq    0.69259E-08   -8.1595 0.69259E-08   -8.1595 0.10000E+01    0.0000
  -- species omitted here --
 175 ZnCl3-       0.94075E-07   -7.0265 0.50310E-07   -7.2983 0.53478E+00   -0.2718

  Charge balance for all species = -.1125E-03

    Component            Molality      Aq.molality       ppm     log[A(N)/A(H+)**Z]
                                         (total)
     1 H+             0.6402323E-05  0.2806731E+00  0.2587066E+03      0.0000
     2 H2O            0.1000000E+01  0.5522772E+02  0.9098519E+06      0.0000
     3 Cl-            0.1097458E+01  0.1341035E+01  0.4347755E+05      5.2560
     4 SO4--          0.1481587E-03  0.1636928E-03  0.1437975E+02      5.8784
  -- species omitted here --
    22 H2AsO3-        0.1177059E-05  0.1124963E-03  0.1285277E+02     -0.6085

    Component          Tot moles       Aq. moles       Solid moles     Gas moles

     1 H+             0.3234352E+00   0.3234460E+00   -.1080840E-04   0.0000000E+00
     2 H2O            0.6364409E+02   0.6364409E+02   0.4053099E-05   0.0000000E+00
     3 Cl-            0.1545400E+01   0.1545400E+01   0.0000000E+00   0.0000000E+00
     4 SO4--          0.1886393E-03   0.1886386E-03   0.6751429E-09   0.0000000E+00
     5 HCO3-          0.3499280E+00   0.3499280E+00   0.0000000E+00   0.0000000E+00
  -- species omitted here --
    22 H2AsO3-        0.1296400E-03   0.1296400E-03   0.0000000E+00   0.0000000E+00

  Chg. balance for solid moles: 0.2938E-20  Mass of aqueous solution: 0.126017E+04 g

  Temperature = 178.25 C   Pressure =  500.00 bar   Mixer frac. =     0.1500000

  Gas or mineral    Moles    Log moles   Grams    Log grams  Wt.percent    Vol(cm3)

  argentite      0.1031E-06   -6.987   0.2556E-04   -4.592   0.3102E+01   0.3589E-05
  galena         0.1011E-05   -5.995   0.2419E-03   -3.616   0.2937E+02   0.3184E-04
  muscovite      0.6760E-06   -6.170   0.2692E-03   -3.570   0.3268E+02   0.9521E-04
  sphalerite     0.2919E-05   -5.535   0.2844E-03   -3.546   0.3452E+02   0.6955E-04
  bornite        0.5401E-08   -8.268   0.2710E-05   -5.567   0.3290E+00   0.5332E-06

  Gas or                            Partial press.   Fugacity coef   Log fugacity
  Mineral          Mole fraction     or activity     Activity coef   Log activity

  argentite          0.1000E+01       0.1000E+01        1.0000          0.000
  galena             0.1000E+01       0.1000E+01        1.0000          0.000
  muscovite          0.1000E+01       0.1000E+01        1.0000          0.000
  sphalerite         0.1000E+01       0.1000E+01        1.0000          0.000
```

```
bornite           0.1000E+01        0.1000E+01         1.0000          0.000

Total fraction of mixing solution added:     0.1500000

Solid products produced:  Mass =    0.000824 g     Volume =    0.000201 cm3
  WARNING: mineral volume may be in error because some mineral densities
  were not supplied in SOLTHERM.  See mineral list in file Skip_Species.txt.
   Estimated lowest electrum affinity for X gold = 0.300
    AFFINITY:  0.2107E+03
    GOLD Q/K:      0.0390
    SILVER Q/K:    0.3161


Gas composition at saturation (  3 iterations)
-----------------------------------------------
Temperature:      178.2522 deg.C
Sat. pressure:     63.3633 bar

     Gas          Mole fraction    phi     Fugacity     Partial P(bar)

   H2O,gas          0.2407E+00   0.7308   0.1114E+02    0.1525E+02
   CO2,gas          0.7593E+00   0.9270   0.4460E+02    0.4811E+02
   CH4,gas          0.2204E-07   1.0879   0.1519E-05    0.1397E-05
   H2,gas           0.2372E-05   1.0283   0.1546E-03    0.1503E-03
-- species omitted here --

NON-Ideal mixing with H2O, CO2, CH4 Gases

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

The following gases and minerals are presently in matrix or were just added

Gas or Mineral      Log K   Log Q  Log(Q/K)  Log(Q/K)/S  Affinity  Log Fugacity

 37 argentite      -23.00  -23.00    0.00       0.000   0.00000E+00
 50 bornite        -74.69  -74.69    0.00       0.000   0.00000E+00
104 galena         -10.44  -10.44    0.00       0.000   0.00000E+00
147 muscovite       -4.53   -4.53    0.00       0.000   0.55037E-11
192 sphalerite      -9.74   -9.74    0.00       0.000   0.00000E+00

The following gases and minerals are presently EXCLUDED from matrix
  (Gases and minerals with log(Q/K) less than -5 are not listed below)

Gas or Mineral      Log K   Log Q  Log(Q/K)  Log(Q/K)/S  Affinity  Log Fugacity

  1 H2O,gas          1.63   -0.02   -1.65      -1.652   0.34121E+04    1.047
  2 CO2,gas         -6.32   -7.36   -1.05      -0.350   0.21680E+04    1.649
  3 CH4,gas          5.49   -3.03   -8.52      -2.129   0.17593E+05   -5.818
  4 H2,gas           7.58    1.08   -6.51      -3.720   0.13446E+05   -3.811
  5 H2S,gas         -5.63  -11.69   -6.07      -3.033   0.12528E+05   -3.366
-- species omitted here --
 11 acanthite      -22.83  -23.00   -0.17      -0.043   0.35628E+03
 12 acmite           5.80    3.10   -2.70      -0.312   0.55671E+04
 16 albite-high     -1.64   -2.76   -1.12      -0.102   0.23190E+04
 17 albite          -2.08   -2.76   -0.68      -0.062   0.14087E+04
 21 andalusite      -0.21   -2.93   -2.72      -0.227   0.56177E+04
-- species omitted here --
219 wollastonite     8.38    4.10   -4.28      -0.856   0.88369E+04
220 pseudo-wolla     8.82    4.10   -4.73      -0.945   0.97616E+04
221 wurtzite        -8.23   -9.74   -1.51      -0.504   0.31248E+04
222 zincite          6.14    1.93   -4.21      -1.051   0.86869E+04

Calculations done for   178.2522 Deg. C;    500.0000 bar

Mixer fraction:     0.150000

                            Temperature   Stoc.ionic strength  Heat per mole

Actual solution:           178.252            .15160E+01         14.102
Mixing solution:            25.000            .50000E-10          2.703

Fract. of mixing solution added:   0.050000
      BITMOL = 0.2775E+01  OLDMOL = 0.6538E+02

New heat:     13.638     New temperature: 172.152

New mixer fraction:     0.200000
Resulting temperature: 172.152Deg. C

Solids and gases carried

Charge balance check after fractionation or titration: TBAL = -.1296E-03
```

[End of equilibration step]

3.5.1 Title Block

The title block contains the title, the number of iterations (loops) used to reach convergence, the electrical charge of the solution, as well as temperature, pressure, enthalpy or mixer fraction, moles of liquid and total water, water activity, stoichiometric and true ionic strength, and osmotic coefficient. The amount of liquid water is the amount of water not including water tied in solids and gases. The mixer fraction matches TOTAL MIXER (see CHIMRUN file), which is the sum of all the mixing increments when mixing is selected (i.e., total grams of titrated rock, total moles of titrated reactant mineral, total grams of titrated aqueous phase, etc.).

3.5.2 Speciation results

The molalities, activites and activity coefficients of aqueous species are listed, wherein H^+ is the first one. pH is not specifically output, but can be read in the Log Activity column for H^+. Aqueous species with molalities less than SUPRNT (specified in CHIMRUN file) are not printed. The molalities listed for each individual species are the final, converged values of the TRIAL MOLALITY values (mtry's) which are supplied in the CHIMRUN file.

3.5.3 Component distribution among phases: solids, gases, aqueous

If gases or minerals are saturated, a summary of the composition of the chemical system follows the speciation data. The *Molality* column is as described above. The *Total moles* column defines the composition of the system and indicates the total moles of component species in the chemical system, which changes relative to the initial input in a titration or mixing run. The "total moles" value for a given component species contains the sum of the molar amounts of all aqueous species, minerals, and gases containing that species. The *Aq. moles* column contains the total moles of species in the aqueous phase only, computed by subtracting *Solid moles* plus *Gas moles* from *Tot moles*. Beware, *Aq moles* do not necessarily refer to one kilogram of water. In contrast, the *Aq. Molality (total)* column does. The *ppm* column indicates parts per million of total aqueous species, computed from the *Aq. molality*. The *Solid moles* column indicates the total quantity of each component contained in saturated minerals. The *Gas moles* column indicates the total quantity of each component contained in saturated gases.

3.5.4 Mineral and gas quantities

For saturated minerals and gases the *Moles* and *Grams* columns indicate the amounts of minerals and gases in the saturated assemblage. The *Moles* column contains the converged values of Mintry provided in the MINERALS column in the CHIMRUN file. The *Mole Fraction* column indicates the mole fractions of end-members in mineral solid solutions, or the mole fractions of gases in the saturated gas phase. If no gases or mineral solid solutions are saturated, or if LIMSOL is set to 0 (see CHIMRUN file), mole fractions are unity (1). The *Wt. percent* column indicates the weight percent of gases and/or minerals in the equilibrium assemblage and are computed separately for gases and minerals. The weight percent of gas given in some runs is the proportion of total gas mass to the total mass of the chemical system (aqueous, solid, and gas). If the mixing option (coolbrew) was selected, the total fraction of mixing solution added is also indicated. This value is the same as that indicated in the title block.

If non-ideal mineral solid solutions (e.g. electrum) are included in the calculation but are not saturated, the composition at which their affinities are the smallest are also printed. If this affinity becomes negative, the solid solution saturates. Similarly, if gases are not saturated and if the IPSAT option is enabled (see CHIMRUN file), the composition of the gas phase at saturation

is printed. The "*number of iterations*" given with this output indicates how many iterations were used to solve for the gas composition at saturation and for the saturation pressure, and is not related to the total number of iterations required to compute the current equilibrium assemblage. Boiling occurs when the the calculated gas saturation pressure reaches the current pressure.

3.5.5 Mineral saturation conditions

It is valuable to know what minerals are undersaturated and by how much, so this information is provided near the end of the results for each equilibration, although these data may be suppressed with *istep* set to 0. For each mineral, solid solution end member and gas component of a (potential) gas phase, the following information is output: the gas index and name; the equilibrium constant, *Log K* (from SOLTHERM); the activity quotient, *Log Q;* the saturation index, *Log(Q/K)*; the scaled saturation index, *Log(Q/K)/S*, which is the saturation index divided by the total number of component species contained in the stoichiometry of that phase (Reed, 1998); the *Affinity* (-RTlog(Q/K)), and the *Log Fugacity* (for gases only). Only minerals with Log(Q/K) between -5 and +5 are printed. Gas fugacities are given by: log(fugacity) = Log(Q/K). Notice, however, that for gases included in a gas mixture (JSOLS = 6, see SOLTHERM data file in Appendix A), the values of K indicated in the LOG K column and used to compute Log(Q/K) are actually the product of K x pressure, as explained by Reed (1982, 1998) and Reed and Spycher (1989).

The minerals and gases currently saturated or supersaturated in the chemical system are indicated on output as "presently in matrix or just added". Undersaturated phases are included in the list of phases "presently excluded from matrix".

3.5.6 Conclusion of equilibration information

At the end, the fractionation option, IFRAC (see CHIMRUN file), causes printing the following messages: Solids and gases carried, for no fractionation; Solids and gases left behind, for fractionation of all phases; Solids only left behind, for fractionation of solids only. If the mixing option is selected, BITMOL and OLDMOL are output. These variables are the molar amounts of water plus salt in the mixer solution and the current solution, respectively.

The complete output file described above is repeated for each calculation step. For plotting purposes, a condensed version of this output file is also created (see next section).

3.5.7 Extended output

If the ISTEP is set to 1in the CHIMRUN file, additional data is provided in the output for debugging, including the matrix of partial derivatives of mass-balance and mass-action equations after the first and second iterations, aqueous species data after the second iteration, and, at each iteration, the ionic strength and the molality of each component species, followed by a dump of the array containing the change in TRIAL MOLALITY (mtry) values from the previous iteration to the current one. Mtry differences become very small as CHIM converges. If the ITREF option in CHIMRUN is set > 0, the residuals of the mass-balance and mass-action equations are also output.

3.6 The plot file CHIMPLOT.DAT (IPUN)

CHIMPLOT.DAT is created if IPUNCH in the CHIMRUN file is non-zero. The file contains a condensed version of the calculation results to be used for plotting. If a calculation is carried out in more than one pickup run as most are (see chapter 4), plot files for each pickup run must be saved after each run, and appended to each other to make a complete plot file (this plot file can then be read by a plotting program such as MINTAB. For efficiency, aqueous species and gases are stored in fixed length arrays in the plot file, and are identified by their sequence position in these arrays. Therefore, to obtain consistent plot files from one pickup run to another, the total number and the sequence position of aqueous species and gases must not change between pickup runs. This means that aqueous species and/or gases CANNOT be suppressed or rearranged in a different order from one pickup run to another. Saturated phases, however, are stored in a variable length array and are identified by name. Therefore, different minerals may be suppressed or added from one pickup run to another. The format of the plot file is given in appendix B.

4. GETTING STARTED

4.1 Trial Execution

If you have not yet tried the demonstration input files, do it now. See section 1.1

4.2 A Well Reasoned Geochemical Hypothesis

Running CHIM builds knowledge and character. In addition to the personal growth that comes from working through computing hassles, running CHIM provides a geochemical learning experience. It is healthy to try out off-the-wall ideas in CHIM, just to see what one can learn. For example, staring from "I wonder what happens if a volcanic gas condensate reacts with limestone", one can set up a CHIMRUN file containing the gas condensate and the limestone, and let it rip. The output file reveals the changes in pH, metal complexing, and mineral precipitates that develop as the reaction proceeds. By working through the output file, thoughtfully rationalizing why all of the chemical changes occur, one learns about the geochemical process.

In most cases, CHIM serves to test a well reasoned geochemical hypotheses, which is based on a description of a real-world geologic and geochemical environment. A successful and profitable CHIM experience begins with a geochemical hypothesis, which one commonly modifies repeatedly as CHIM reveals thermodynamic constraints. In most cases, the geochemical features of the hypothetical process are complicated and varied, requiring that the process be broken down into a series of steps, each of which CHIM may compute. For example, in a study of sediment hosted copper deposits precipitated from a red bed-derived, metal-bearing brine, it might be appropriate to compute the following steps, each of which calls for a substantial CHIM calculation.

a. Evaporate river water to make brine.
b. React brine with andesite in contact with the atmosphere.
c. Bury the brine-rock system, heat to 150° C, out of atmospheric contact.
d. Extract brine from rock, react with carbon-bearing shale.
e. Extract brine from rock, react with H2S in pore-filling natural gas.
f. Extract brine from rock, react with methane.

4.3 The first run: setting up the CHIMRUN file

One's well reasoned geochemical hypothesis is the starting place for setting up the CHIMRUN file. Before doing anything with CHIMRUN, it is wise to calculate homogeneous equilibrium with program SOLVEQ-XPT on the aqueous solution that is to be used in CHIM. SOLVEQ-XPT is easy to run, and is practical for determining the consistency of the input data, the charge balance of the solution, the speciation of aqueous phase, the supersaturated minerals, and, if pH is given, the total moles of hydrogen ion in solution (TOTAL MOLES H^+), which is necessary in CHIMRUN. Notice that if the composition of the original solution is such that large amounts of solids or gases are supersaturated, the solution is not an appropriate one to begin a CHIM run, because much of the mineralogically interesting and important geochemistry is already fixed by the starting water. SOLVEQ-XPT reveals such a condition and provides guidance in selecting and building a starting water.

After getting the SOLVEQ-XPT output, you are ready to create the run file, CHIMRUN, by (a) running program GEOCAL; (b) editing an old run file that serves as a template; or (c) by starting from scratch (but this is tedious and unnecessary). Generally, the easiest route, once you have your input water composition in molality (by running GEOCAL, for example) is to use as a template an existing CHIMRUN file, used for some other calculation of the same general type that you plan to run (e.g. rock titration, boiling, fluid-fluid mixing, etc.).

GEOCAL is useful for setting up the appropriate formats and to convert analyses in ppm, etc. to molality. GEOCAL interacts with the user, making it easy and straightforward to convert compositions of waters and gases and to set up input files for CHIM (and SOLVEQ-XPT). In most cases, CHIMRUN files created by GEOCAL need to be further edited in order to specify the desired options or to add a reactant to the CHIMRUN file. After running a first equilibration with CHIM, CHIM rewrites the CHIMRUN file with all current data, as described below in this chapter. Both GEOCAL and CHIM write extra records in the CHIMRUN file that contain format indicators and names of input variables. These extra records are used to facilitate editing, and are skipped by CHIM on input (see chapter 3). These extra records must always be present in the CHIMRUN file, or reading errors will result. If you are creating a file from scratch, leave these extra records blank. The formats and variables of all other records must be set carefully, according to the formats described in chapter 3. Following is a general step-by-step procedure for starting any calculation with CHIM.

Select the desired options by giving appropriate values for all input parameters in the CHIMRUN file. These parameters are defined in chapter 3. Chapter 5 provides details on how to set up particular calculations. Although pH can be input, and thereby held fixed throughout the run, it is rare that one would want to hold it at a fixed value, so, most likely, pH should be set to zero (or blank, which is the same in Fortran). If pH is not set, it is computed from an input value of TOTAL MOLES H^+, which is most easily obtained from the SOLVEQ-XPT calculation. Remember to input TOTAL MOLES for water in kilograms.

Do not specify TOTAL MOLES for both bisulfide (SAQ = 6) and oxygen (SAQ = 31) in the same run. In this system of components, the use of both constitutes a set of thermodynamic components that is greater than the minimum number. If both are specified, an error message appears and the run aborts. To decide between them, consider that in oxidized waters, the absolute concentration of sulfide species is so small (less than 10^{-70}) that working with sulfide is much less intuitively meaningful than working with an oxidized species. In oxidized waters, the concentration of aqueous O_2 is substantial, so it can be used in place of sulfide-sulfate to express redox equilibria. This is accomodated in SOLTHERM by the inclusion of two sets of equilibria for redox species and minerals (e.g. Fe^{+++}, Cu^{++}, Au^{+++}, CH_4, hematite, native copper, galena, etc.), one expressed in terms of O_2-H_2O-SO_4^{2-}-H^+ and the other set expressed in terms of HS^--SO_4^{2-}-H_2O-H^+. Thus all redox, sulfide and some oxide species and minerals are listed twice in SOLTHERM. On any given run, however, the user specifies composition of the system only in terms of O_2 or only in terms of sulfide, so CHIM uses only the relevant equilibria out of SOLTHERM.

If fluid-fluid mixing is selected (TEMPC non-zero), the composition of the mixer solution (MIXER TOTAL MOLES) must also be specified. The compositions of the starting solution and of the mixer solution must be expressed in terms of the same component species. (This applies to oxidation too. If you're oxidizing using MIXER TOTAL MOLES in a system that is initially reduced, you express O_2 as: -0.5 HS^- + 0.5 SO_4^{2-} + 0.5 H^+) If a component species is present in only one of the solutions, you must input a value of zero for the amount of the absent species

(note that TOTAL MOLES = 0 for H^+ and HS^- has a meaning for pH and redox calculations, respectively). For TRIAL MOLES values, good approximations are obtained from the SOLVEQ-XPT output.

Once you have specified the composition of the starting solution (TOTAL MOLES) and estimated trial molalities (TRIAL MOLALITY), you need to specify which minerals or gases are in equilibrium with that solution (MINERALS) and in what amounts (MIN TRIAL MOLES). For an original run, the nature and amounts of these phases are unknown. If a prior run with program SOLVEQ-XPT indicates supersaturated minerals, CHIM must equilibrate one or more of these minerals (most likely the most supersaturated ones). You can omit the input of saturated minerals (MINERALS and MIN TRIAL MOLES), and let CHIM equilibrate with the appropriate minerals by itself. If a large number of minerals belong to the equilibrium assemblage, this procedure might consume a lot of computing time, as CHIM would have to sort through many supersaturated minerals. Another possibility is to make an educated guess of which mineral is most likely to belong to the equilibrium assemblage, and input MINERALS and MIN TRIAL MOLES values for these minerals. If a mineral does not belong, CHIM will kick it out. However, if many of the specified minerals do not belong to the equilibrium assemblage, CHIM will fail to converge. As mentioned in a preceding section, it is actually rare that one would want to start a model run with a fluid that is already supersaturated with anything, so if you find yourself in this situation, think it over.

If you're doing a rock titration, as indicated in your run file by inputing a non-zero value for MINSOLV, you must input a reactant rock composition (REACTANTS and WEIGHT PERCENT) following the saturated mineral data in the CHIMRUN file (see chapter 5). If you set MINSOLV to zero, REACTANTS and WEIGHT PERCENT do not need to be specified.

Finally, you can specify at the bottom of the CHIMRUN file the names of the aqueous species, minerals, and gases that you wish to supress from the calculation. You may choose to suppress certain minerals and species because their thermodynamic data are questionable or because their formation is kinetically retarded on the time scale of reactions in your system.

Once all the parameters have been set in the CHIMRUN file, set NLOOP = 0 in that file, and run CHIM. In the output file, CHIMOUT.DAT, you should get a complete dump of all input data, as well as a list of all species (aqueous, solid and gas) in the calculations. At this stage, most errors are likely to be related to input mistakes in CHIMRUN. Check that the run file meets all specifications given in chapter 3, and that all other input and output files are correctly assigned. Check that the areas in CHIMRUN between the title and the option lines, and between the TOTAL MOLES, MINERALS, REACTANTS and MINS TO SUPPRESS data area contain one blank line, followed by a line of format indicators (or another blank line). Also, CHIM has various error messages built into its code that help one determine the source of error (see chapter 6). Once CHIM runs correctly (with NLOOP = 0), double check all input data. Are all the selected options correct (remember that CHIM might reset options that are inconsistent with each other). Are all TOTAL MOLES and MIXER TOTAL MOLES values correct? Are the suppressed species, if any, appropriate? If minerals were given (MINERALS and MIN TRIAL MOLES specified), check the mineral list on the output, and make sure that each of these minerals has a non-zero value equal to MIN TRIAL MOLES in CHIMRUN in the TRIAL MOLES column. Taking time in double-checking input data can save a lot of your own time and frustration by preventing the discovery or a setup error when you think your finished.

Once all input data is double-checked, set NLOOP to 70, and set STEP LIMIT to the current temperature (TEMP), mixer fraction (TOTAL MIXER), or pressure (PFLUID), depending on

which type of calculation is selected (chapter 5). This allows CHIM to run, but stop after the current calculation step is accomplished. Now run CHIM. If any problems occur, refer to chapter 6. If CHIM runs correctly, you should be getting some information at your terminal. The ionic strength after each iteration appears on the screen. Normally, the ionic strength should converge to a constant value after 10 or 15 iterations. If the ionic strength converges but the iterations reach the loop limit NLOOP, you might have given a too-small ERPC. ERPC = 10^{-12} should work without problems. Smaller values are not recommended, but much larger values might lead to apparent convergence. Ionic strength convergence is only an indicator; in some cases, the ionic strength converges, but CHIM still does not converge, even if ERPC is set correctly, because the complete system of equations has not satisfied the stringent convergence test (Reed, 1998). After convergence, the current equilibrated mineral assemblage appears on the screen. This might not be the real equilibration assemblage however, and it might take CHIM more than one equilibration to determine the correct equilibrium assemblage (this especially when starting a new run). Once the correct equilibrium assemblage has been computed, information about the current step, the next step increment, temperature, pH etc. appear on the screen, and CHIM should stop, if you set SLIM to make it stop after one equilibration. Modern personal computers are fast enough that the output to the screen during execution is nearly impossible to read. One may interupt execution and read the output using the "pause" key, or just wait and read it in CHIMOUT.DAT.

After this first equilibration, the CHIMRUN file has been rewriten by CHIM (into CHIMRUN.DAT, the "pickup" file, see next section), and contains all current run conditions. On subsequent runs, this file is repeatedly updated with the results of the last equilibrated runs, as described in the next section. Therefore, you should save the current CHIMRUN file by copying it into another file (commonly using a DOS batch file; see below). This first CHIMRUN file will be useful to restart the calculations from the beginning at a later stage, if desired. After you saved your first CHIMRUN file, set STEP LIMIT to some other limit (e.g. 10 STEP INCREM increments from the current step) and run CHIM again. You are set! This time, CHIM will run until the SLIM step is reached. If any problems arise, refer to chapter 6.

In the next section, the concept of pickup files is described. These files are CHIMRUN files rewriten by CHIM after each equilibration, and are extremely useful to carry out one long calculation in several smaller successive calculations.

4.4 Pickup runs and pickup files

As discussed in the introduction of this manual, CHIM carries out calculations step by step, where each step corresponds to a different temperature, pressure or composition of a chemical system. For each step, the equilibrium assemblage is computed and written to CHIMOUT.DAT and to CHIMPLOT.DAT. A typical run consists of a large number of steps, which are normally broken into groups of steps called calculation "increments" when referring to the body of content in the increment, and are called "pickups" when referring to the execution of the next increment (e.g. we run a pickup file to begin the next increment). (The term "pickup" is the term applied by Helgeson to the same process in running the original PATHCALC). For example, in a cooling temperature change calculation, the temperature steps may be one degree (in STEP INCREM) and calcultion increments may be 20 degrees, meaning the program is allowed to execute through 20 degrees of cooling before stopping at the stopping temperature designated by STEP LIMIT.

To prepare pickups, the run file, CHIMRUN.DAT is automatically updated by CHIM after

each equilibration. If the current equilibration is the last equilibration for the current step (i.e., overall equilibrium has been reached for the current T, P and composition (X), as opposed to an intermediate, metastable equilibrium), the input data are saved in the file CHIMRUN.DAT. If the current equilibration is not the last for the current step, the input data are saved in the file CHIMRUN.SAV. Because these updated "pickup" files contain the correct TOTAL MOLES, TRIAL MOLALITY, GAMMA, and MIN TRIAL MOLES values for a given equilibration, convergence is reached easily when a run is picked up. An inconvenience with this method is that one must copy the CHIMRUN file onto an other file to save the current version. The use of a DOS batch file to address this inconvenience is outlined below.

Users should always save the pickup file for the first step of any calculation (CHIMRUN.sta; see below), since many times, for various reasons, one might wish to restart the calculation from the beginning. Notice that if CHIM is interrupted after an equilibration that is not the last one for the current (T,P,x) step, it is neceassary to copy the last pickup file CHIMRUN.SAV into CHIMRUN.DAT to run CHIM with this last pickup file.

4.5 Batch files for CHIM execution

Keeping track of files for output, plotting, starting input and input pickup can be a pain. To simplify the process, two types of batch files are uesful, which we choose to call "Chil.bat" and "xyz.bat", where "xyz" is s run name that is different for each calculation. (Although “batch files” originated in the DOS command line era, they persist under Windows XP and Windows 7 unchanged, except that “DOS” *per se* is no longer in the picture, however identical use of the “command prompt” is. The command prompt is accessible under “accessories” in Windows, and the DOS commands such as “copy”, “delete”, “dir”, “cd”, etc. exist as ever.) Batch files contain instructions that are executed as a program when the name of the batch file is executed at the command prompt; e.g. one types "chil <enter>" to execute the chil.bat file. Users create these files themselves using a text editor. Recommended contents for these files follow.

file: *chil.bat*
```
copy CHIMRUN.bak CHIMRUN.ba2
copy CHIMRUN.DAT CHIMRUN.bak
c:\xxx\CHIM
```
(where "xxx" refers to the path to the CHIM.exe file)

Run chil.bat to make CHIM execute, using the current CHIMRUN.bat file for starting input. The second line of chil.bat saves the current CHIMRUN file into a backup file called CHIMRUN.bak. The first line of the chil.bat file saves the previously backed up start file to a second backup file called CHIMRUN.ba2. Once these two files are saved, the third line actually executes CHIM.

file: *xyz.bat*
```
copy CHIMRUN.DAT xyzrun.%1
copy CHIMOUT.DAT xyzout.%1
copy CHIMPLOT.DAT xyzplt.%1
```

Run the xyz.bat file to save each of the critical files for the current calculation increment. The

three DOS commands copy the CHIMRUN, CHIMOUT and CHIMPLOT files from the last increment into files named for the current calculation with file types that the user increments to create a sequential file series. The user defines the sequence by inputting a number (e.g. d01, d02, ...d0n) each time the xyz batch file is executed; the sequence number automatically replaces the "%1" variable in the batch file. For example, after the first increment is finished, type "xyz d01" to save the current CHIMRUN.DAT file to the name "xyzrun.d01", to save CHIMOUT.DAT to "xyzout.d01" and to save CHIMPLOT.DAT to "xyz.d01". After completion of the next increment, type "xyz d02", etc.

The "xyz" name should be a the user decides that has meaning for identifying the model run. For example, we have used "but1" in place of "xyz" to idnetify the first calculation of a series on intended to model processes in the Butte hydrothermal system; the second calculation on Butte was named "but2", etc.

Once the whole calculation is completed, one has saved on disk a set of sequentially named input, output and plot files for the calculation. The plot files are then normally concatonated into a single plot file, named "xyz.sum" for execution of the mintab plotting program. See below.

4.6 Selection of saturated phases: LOOC, SOLMIN and LIMSOL options

At any given step, CHIM determines which phases (minerals and gas) belong in the equilibrium assemblage. The basic approaches and details of phase selection are discussed by Reed (1982), Spycher and Reed (1988) and Reed (1998). CHIM determines the phase assemblage starting by computing the saturation indexes (log Q/K) of minerals not currently equilibrated with the solution. If one or more minerals are supersaturated (log Q/K > 0), CHIM does one of the following: a) equilibrates with the most supersaturated mineral, if LOOC is set to zero in the CHIMRUN file, or b) backsteps (by half of the last step size) until only one mineral is supersaturated, if LOOC is non-zero. Backstepping can be applied, but it is rare that this is a better choice than cutting the step size for the whole run (setting SINC to a smaller value in CHIMRUN.DAT), thereby preventing the simultaneous saturation with a large number of minerals. The latter is bad because one loses information about the sequence of saturation of these minerals. Also, CHIM might encounter convergence problems (see chapter 6) if it has to sort through too many supersaturated minerals.

If a mineral belongs to an ideal solid solution and LIMSOL is nonzero, CHIM equilibrates with the solid solution if the sum of the log Q/K's of the endmembers exceeds one (in an ideal solid- solution, the log Q/K of an endmember is equivalent to the mole fraction of the endmember in the solid solution; for ideal mutisite mixing, log Q/K is actually raised to a power related to the soichiometry of the endmembers; see Reed, 1998). For a non-ideal solid solution (currently only electrum), CHIM selects the solid solution to join the phase assemblage if the weighted average of the affinities of the endmembers is zero, or smaller, for any particular composition of that solid solution. For a gas phase, CHIM selects the gas phase if the sum of the partial pressures of the gas endmembers is greater than or equal to the total pressure (for an ideal gas, the partial pressure is equivalent to log Q/K; for non-ideal gases, the gas partial pressures at saturation are computed by Newton-Raphson iterations if IPSAT is set to 1).

Detecting newly undersaturated pure phases is straightforward. If a pure mineral becomes undersaturated, its computed molar amount becomes negative. Computed negative amounts of pure phases do not create numerical problems. If the SOLMIN option is disabled (SOLMIN = or > 0), CHIM computes equilibrium, identifies phases with negative mass, if any, remove these

phases from the equilibrium assemblage, and recomputes equilibrium. Because this process always requires an additional calculation of equilibrium without the "negative minerals", the SOLMIN option was added in CHIM. The SOLMIN option is enabled if SOLMIN is set to a negative value (e.g. -1.E-8) in the CHIMRUN file. If SOLMIN is less than zero and if, after the fifth iteration, the computed molar amount of any pure saturated phase is smaller than SOLMIN, CHIM throws out that phase before convergence is reached.

The advantage of the SOLMIN option is that undersaturated minerals are thrown out as soon as they are detected, easing convergence and avoiding an additional calculation of equilibrium. The disadvantage of the SOLMIN option, however, is that minerals that should stay saturated might be removed prematurely from the equilibrium assemblage. This can happen in numerically difficult cases, where the calculated amount of one or more saturated minerals might become negative for a few iterations, but then become positive again as convergence nears. In such cases, these minerals are thrown out by mistake. Since these minerals do belong to the equilibrium assemblage, their saturation indexes become greater than zero and CHIM picks them up again on the next equilibration. This might result in minerals being swapped indefinitely in and out of the equilibrium assemblage. Also, with the SOLMIN option enabled, an incorrect mineral removal or a convergence problem might result in the "cascade" removal of a lot of other saturated minerals, resulting in a convergence failure. These problems can be circumvented by setting SOLMIN to a more negative value. If problems still arise with large negative SOLMIN values, this option should be disabled (by setting SOLMIN>0), or the calculation should be restarted with smaller steps. The SOLMIN option is "touchy", and beginners should disable it. However, in complicated systems, this option has proven to be extremely useful to help reach convergence.

Solid solutions cause headaches. Detecting undersaturation of solid solutions or mixed gases is more difficult than with pure phases, mainly because equilibration with negative endmember amounts is numerically and theoretically impossible. For these reasons, negative amounts of solid solution endmembers computed during the iteration process are always reset by CHIM to small positive values (currently 10^{-20}). Therefore, if a solid solution end member or a gas in the mixed gas phase becomes undersaturated, its computed amount becomes infinitesimally small, which causes convergence problems in CHIM. In some such instances, it is necessary for the user to identify the problem an fix it by hand by removing the offending solid solution end member (detected by identifying a solid solution mole number, n, equal to 10^{-20}). Usually, the LIMSOL=2 option, below, takes care of the problem.

If LIMSOL is set to zero, all solid solution endmembers are treated by CHIM as pure independent phases, as descibed above. If LIMSOL is set to 1, undersaturating solid solutions or mixed gases can only be detected if their amounts decrease from one step to the next, up to a point where convergence fails. The solid solution suspected to undersaturate must then be removed "by hand" from the pickup file CHIMRUN, and CHIM must be run again (see also chapter 6). To circumvent the impractical "hand removal" of undersaturating solid solutions, the LIMSOL = 2 option was added in CHIM. With LIMSOL set to 2, CHIM automatically removes endmembers whose computed trial amounts are less than zero after six iterations. CHIM also removes endmembers that become too small in mass while keeping other endmembers that have significant mass. The disadvantage of the LIMSOL = 2 option, as with the SOLMIN option discussed above, is that endmembers that should stay in the equilibrium assemblage might be mistakenly removed, causing convergence problems in some cases.

In contrast to pure phases, if a solid solution endmember has been removed from the

equilibrium assemblage, but other endmembers of the same solid solution are still in the equilibrium assemblage, CHIM will no longer recognize the removed endmember as part of a solid solution, and CHIM will NOT pick it up again, unless it independently supersaturates as a single phase. Therefore, if CHIM removes an endmember present with significant mass, make sure that CHIM did not remove this endmember by mistake, and try running CHIM again after re-inserting the removed endmember "by hand" in the current CHIMRUN data file. If a complete solid solution undersaturates (if CHIM removes all endmembers from the equilibrium assemblage) CHIM will pick it up again if it was kicked out by mistake, or if it becomes supersaturated again. The LIMSOL = 2 option has its advantages, but might create problems for inexperienced users. If you are not yet familiar with CHIM and with the numerical problems inherent to computing heterogeneous equilibrium, set LIMSOL to 1, or ignore solid solutions altogether by setting LIMSOL to zero.

5. TYPES OF CALCULATIONS WITH CHIM

CHIM is capable of executing a very broad range of calculation types. Each calculation type has its own particularities and is described below. The input parameters discussed in this chapter are described in chapter 3.

5.1 Cooling and Heating

Cooling and heating calculations are the easiest ones to do. The temperature change step is given by SINC, which is positive for heating, or negative for cooling. To start a heating or cooling run (at constant pressure), the starting temperature TEMP should be given, as well as STEP INCREM and STEP LIMIT. CHIM will stop once the temperature reaches SLIM (the current temperature range of thermodynamic data is from 25 to 340 C). TEMPC and INCRP must be set to zero, and the pressure curve data file (curve.dat) must be empty or unassigned. MIXER TOTAL MOLES values should be zero, although non-zero values have no effect.

If you desire to compute the saturation pressure of gases at each temperature step, set IPSAT to 1. Note that if one is heating a solution, the saturation pressure might reach the designated fluid pressure, PFLUID, and a gas phase will form (if IPSAT is zero, gases will saturate only if the sum of their fugacities equals PFLUID). If gases saturate, additional temperature increments at constant pressure might cause excessive boiling and convergence might fail because the liquid phase is completely exhausted (see boiling section below). For heating and cooling, as for almost all other types of calculations, set PH to zero and input an TOTAL MOLES value for H^+. If TOTAL MOLES is not known, CHIM will calculate it from a known pH at a given temperature. In order to do so, set pH to the known pH; then TOTAL MOLES for H^+ will be computed. As an alternative, SOLVEQ-XPT may be used to compute TOTAL MOLES for H^+ (see chapter 4).

5.2 Boiling and Condensing

There are five ways to compute boiling with CHIM: 1) boiling with enthalpy constraint, 2) boiling following a series of T-P points read from the T-P CURVE DATA block in CHIMRUN, 3) isothermal boiling, and 4) isobaric boiling. Gas condensation can be carried out by reversing any of the boiling calculations.

5.2.1 Boiling with enthalpy constraint. Boiling with enthalpy constraint is the most appropriate way to compute boiling. In such calculations, temperature and total enthalpy are given, and CHIM solves for the pressure at which the aqueous and gas phases are in such amounts that that the sum of their respective heats equals the total enthalpy. (Spycher and Reed, 1988). Currently the heat of the aqueous phase is calculated as the heat of pure water at the given temperature, and at the saturation pressure of pure water. The heat of the gas phase corresponds to the heat of an ideal or non-ideal mixture (depending on the IDEAL option) of H_2O, CO_2, and CH_4 gases.

The easiest way to start a boiling calculation with enthalpy constraint is to run CHIM at a given temperature TEMP, setting STEP LIMIT = TEMP so that no temperature increment takes place, and setting PFLUID to a high value (e.g. 500 bars) so that the solution does not boil, and IPSAT to 1. From the output (CHIMOUT.DAT, at full equilibration), find the gas saturation

pressure of the solution at the given temperature. Reset PFLUID in the pickup file CHIMRUN to a value barely lower than the saturation pressure (e.g. decrease the 3rd digit to the right of the decimal point by two units), set ENTH, SENTH and DENTH to 0, and leave TOTWAT at its default value (or 0). Make sure that both IPSAT and IENTH are set to 1, set STEP INCREM to -5, for example and STEP LIMIT to some value lower than TEMP. Run CHIM again. This time, CHIM will equilibrate with the gas phase, and start boiling following STEP INCREM temperature drops, adjusting the pressure, PFLUID. Because ENTH was set to zero, CHIM sets the current total enthalpy ENTH equal to the enthlapy of the aqueous phase at the given temperature. Because the starting total enthalpy SENTH was zero, CHIM sets SENTH equal to the current total enthalpy ENTH. Because DENTH was set to zero, the total enthalpy stays constant, thus boiling is isoenthalpic.

To change the total enthalpy as boiling proceeds, use either DENTH or set INCRP = 2. If DENTH is used, INCRP must be zero, DENTH must be input in kcal/degree, and the step size STEP INCREM must be given in temperature increments; thereby the heat change for a step is calculated as STEP INCREM x DENTH. From one step to another, the current total enthalpy is changed from ENTH to ENTH + STEP INCREM x DENTH (therefore, for heat loss as temperature decreases, DENTH must be positive and STEP INCREMENT negative (negative temperature change). Note that SENTH is used to keep track of the starting enthalpy.

The INCRP = 2 option is used only for isothermal boiling calculations. With INCRP = 2, the temperature stays constant, and the step size STEP INCREM is used to increment enthalpy. STEP INCREM must therefore be input in kcal, and the total enthalpy will change from ENTH to ENTH + STEP INCREM at each calculation step. With the Incrp = 2 option, TOTAL MIXER is also used to keep track of how many enthalpy increments, STEP INCREM, have been added to the system (for a closed system, TOTAL MIXER = ENTH). Use only DENTH or STEP INCREM values that keep the total enthlapy within reasonable limits. If the enthalpy is too high, all the solution will boil, and CHIM will bomb. If the enthalpy is too low, all gases will condense. Steam tables are useful to approximate reasonable enthalpy values. If the system has more than 90 weight percent of gases, TOTWAT should be reset to higher values, or convergence will fail. CHIM will experience problems if more than 99 % of the solution is boiled. For some particular systems, this limit might be lower.

The advantage of the enthalpy constraint is that virtually all cases of boiling can be modeled. If gas fractionation is selected (IFRAC set to 1), Raleigh fractionation will occur. The gas heat is also fractionated. One minor inconvenience of the enthalpy constraint in CHIM is that although you can set temperature and enthalpy, and solve for pressure, you cannot set pressure and enthalpy, and solve for temperature. This is possible in principle, but requires much more programming to accomodate solving for temperature as an unknown (because we need to compute temperature derivatives of all equations).

5.2.2 Isothermal and isobaric boiling. Isothermal boiling without enthalpy constraint can be modeled by setting Incrp to 1. This causes the pressure to change by STEP INCREM at the constant temperature, TEMP. As long as no gas phase is saturated, changing pressure does not affect the equilibrium assemblage. As Incrp is set to 1, IENTH must be 0, and IPSAT should be 1. As the pressure decreases at constant temperature, more and more gas will form and suddenly, all the solution might boil, causing CHIM to diverge (isothermal boiling is the equivalent to adding a lot of heat to the system, so that the whole system may boil to dryness).

Isothermal boiling with enthalpy constraint is modeled by setting Incrp to 2, as well as IENTH

to 1, as described in the previous section on boiling with enthalpy constraint. In such case, enthalpy is incremented with STEP INCREM, at a constant temperature TEMP and changing pressure. In this way, isothermal boiling calculations can be handled much more easily than without the enthalpy constraint. At low temperatures, and for nearly pure water systems, this is the only way to model isothermal boiling.

Isobaric boiling without enthalpy constraint is modeled simply by heating the solution at a constant pressure, providing that the pressure of the system is low enough so that it boils. Set Incrp and IENTH to 0, and IPSAT to 1. As for isothermal boiling without enthalpy constraint, CHIM will quickly diverge upon isobaric boiling, because all the solution will rapidly boil to dryness. Unfortunately, CHIM cannot be used to model isobaric boiling with enthalpy constraint because this requires a whole additional set of derivatives with respect to temperature that we have not programmed.

5.2.3 Boiling following a preset T-P curve. The pressure curve data block (T-P CURVE DATA) in CHIMRUN is required for boiling along a preset T-P curve. This boiling option is enabled if the data block contains at least one T-P point and is correctly assigned. This option should be used only if you want to follow a given T-P curve. Set IPSAT to 1, and INCRP to 0. Set TEMP to any temperature. CHIM will interpolate between the two nearest T-P points in the pressure curve file, and return the appropriate pressure. The major inconvenience of this method is that, depending on the chemical system and on the preset T-P curve, the system might boil too much, or condense entirely. At some temperatures and pressures specific to each chemical systems, the amount of saturated gas phase may vary enormously over extremely small temperature and/or pressure intervals. This might cause convergence problems in CHIM. This boiling calculation option is a remnant of earlier versions of CHIM, and is not very useful since the enthalpy constraint option was incorporated in the program.

5.2.4 Condensation. Gas condensation calculations can be carried out by reversing any of the boiling calculations disscussed above. The easiest way to model gas condensation is to cool at constant pressure. If you wish to condense only the gas phase obtained from a previous boiling calculation, express the gas phase composition (obtained from the boiling run) in terms of component species, and create a new CHIMRUN file with TOTAL MOLES values containing the gas composition (thus excluding the aqueous phase that is in equilibrium with this gas phase). The easiest way to obtain these TOTAL MOLES values is to read them from the "GAS MOLES" column in the CHIM output from your boiling run. If IENTH was set to 1, reset it to 0 to disable the enthaply constraint. Because the composition of the system now corresponds to the composition of the gas phase only, one cannot run CHIM at the same temperature and pressure as those of the system equilibrated with the aqueous phase (if you do so, CHIM will fail to converge as the entire system will boil). Set TEMP to a slightly lower temperature and PFLUID to the same value as for the equilibrated aqueous-gas system. If convergence problems arise, lower the temperature even more. Once CHIM equilibrates successfully, the temperature can be decreased using STEP INCREM, keeping the pressure, PFLUID, constant. The aqueous phase in this condensation calculation will correspond to the gas condensate, and the gases to the "non-condensible gases".

5.3 Fluid-fluid Mixing ("Coolbrew" calculations)

The fluid-fluid mixing option is enabled by setting TEMPC to a non-zero value. This causes CHIM to titrate a mixer solution of composition given by MIXER TOTAL MOLES into the current solution of composition given by TOTAL MOLES. The composition of the mixer solution must be in moles, except for water, MIXER TOTAL MOLES(2), which must be in kilograms (see chapter 3), thus a simple listing of composition in molality can be input as is, using a value of 1.0 (kg) for H_2O. (Rarely, the mass of H_2O might depart slightly from 1.0 for unusual compositions containing abundant hydroxide, for example.)

The "mixer solution" can be an aqueous solution or solids or gases, or any chemical compound whose composition can be expressed in terms of the current component species in SOLTHERM. For example, CO_2 can be expressed as:

$$CO_2 = H^+ + HCO_3^- - H_2O$$

Therefore, to react a solution with CO_2, we first specify the composition of one mole of CO_2 as follows:

MIXER TOTAL MOLES(1) = 1.0 Positive 1 mole of H+ in one mole of CO_2
MIXER TOTAL MOLES(2) = -0.01802 Negative 1 mole of H_2O (0.01802 Kg) in one mole of CO_2. Remember, MIXER TOTAL MOLES for water must be in kilograms.
MIXER TOTAL MOLES(3) = 0 No Cl^- in CO_2.
MIXER TOTAL MOLES(4) = 0 No SO_4^{2-} in CO_2.
MIXER TOTAL MOLES(5) = 1.0 Positive 1 mole of HCO_3^- in one mole of CO_2.
MIXER TOTAL MOLES(6,etc..) = 0 No other components in CO_2

The titration increment STEP INCREM is a fractional unitless factor, by which MIXER TOTAL MOLES values are multiplied before being added to the current solution (TOTAL MOLES values). That is, from one step to the next, TOTAL MOLES values change from TOTAL MOLES to TOTAL MOLES + STEP INCREM*MIXER TOTAL MOLES. For example, if MIXER TOTAL MOLES values represent one mole of CO2, STEP INCREM = 1 will titrate 1 mole of CO2 at a time, STEP INCREM = 0.001 will titrate 1 millimole of CO_2, and so on.

TOTAL MIXER is the sum of all previous STEP INCREM values, and represents the total fraction of mixer solution already added to the original solution. In the example above, 10 increments of STEP INCREM = 0.001 will give TOTAL MIXER = 0.01, or 10 millimoles. At the start of a mixing calculation, TOTAL MIXER must therefore be set to 0. If you choose to titrate the mixer solution in units of kilograms instead of moles, simply specify the composition in MIXER TOTAL MOLES in moles of components in one kilogram of the solution. Then, if you set STEP INCREM to .01, for example, one titration increment will be .01 kilogram (or 10 grams), and the units of TOTAL MIXER will be kilograms. This system may seem a bit confusing, at first, but it is completely flexible. Use it to suit your needs.

If a component species is given in TOTAL MOLES, but does not belong to the mixer solution, its MIXER TOTAL MOLES value must be set to zero. If a component species is given in MIXER TOTAL MOLES, but does not belong to the starting solution, an TOTAL MOLES value of zero must be input. This might result in underflow errors on the first step (TOTAL MIXER = 0), unless the INCREM = 1 option is specified. ICREM = 1 causes immediate

titration of the mixer solution, that is skip the TOTAL MIXER = 0 step. Note that if fractionation is specified (IFRAC non-zero), immediate titration by setting INCREM = 1 is not allowed. If zero TOTAL MOLES values create problems, you can still compute equilibrium at the start of the titration (TOTAL MIXER = 0), by specifying small TOTAL MOLES values instead of zeros (e.g. 10-15). In some cases, however, very small TOTAL MOLES values might create more convergence problems than zero values.

If the mixer solution is not aqueous (does not contain H_2O), TEMPC must be set *exactly* equal to TEMP. If the mixer solution is an aqueous solution, its temperature is given by TEMPC, and CHIM calculates the temperature change upon mixing, if the starting and mixer solutions have different temperatures. These calculations are referred to as "Coolbrew" calculations, after an earlier incarnation of CHIM for mixing that was called COOLBREW. Coolbrew calculations are accomplished in two different ways, depending on the type of calculation, as described below.

If modeling the mixing of two aqueous solutions with no gas phases involved, CHIM interpolates the enthalpies of both solutions from a table (H = f(P, T)) of water enthalpy read from the SOLTHERM data file (between the activity coefficient and the component species data, see appendix A). The resulting temperature after mixing the enthalpies is then interpolated from the same water enthalpy table in SOLTHERM but where P is constant and thus T = f(P, H). Note that these interpolations are used only for mixing calculations, and are not used in the boiling calculations with enthalpy constraint.

If modeling the mixing of an aqueous solution into a boiling solution with enthalpy constraint, CHIM computes enthalpy balance between the boiling solution and the mixer solution. In addition to the change of composition of the system (from TOTAL MOLES to TOTAL MOLES + STEP INCREM*MIXER TOTAL MOLES), the total current enthalpy of the system is also changed from ENTH to ENTH + STEP INCREM*MIXER TOTAL MOLES(2)*ENTHW, ENTHW being the enthalpy of the mixer solution. Mixing of a cold solution into a hot boiling solution, for example, will result in the resorbtion (condensation) of the gas phase at a constant temperature and nearly constant pressure (note that pressure, and not temperature, is left floating in boiling calculations with enthalpy constraint; see previous section). For this type of mixing calculation, enthalpies are calculated from a special routine in CHIM, which computes the enthalpy of pure water. Once all the gas phase is resorbed, CHIM will proceed computing fluid-fluid mixing and temperature change as described in the previous paragraph.

5.4 Water-rock Reactions (MINSOLV option)

The water-rock interaction option in CHIM was formerly only in CHIM's parent, MINSOLV, thus the option name. The Minsolv option is enabled if MINSOLV is set to a non-zero value (MINSOLV values can be 0, 1, 2, 3, or 4, as discussed below). If by mistake, this option is enabled and the fluid-fluid mixing option is also enabled (TEMPC non-zero), CHIM will reset MINSOLV to zero and compute fluid-fluid mixing. Therefore, make sure that TEMPC is set to zero before starting a water-rock interaction calculation.

If MINSOLV is non-zero, CHIM reads the names and amounts of reactants in the CHIMRUN file (REACTANTS and WTPC), and CHIM reads the MINOX data file, which contains reactant stoichiometries (see chapter 3). The reactants specified in the MINOX data file may be any chemical compounds that can be expressed in terms of the component species for a given calculation. Generally, but not necessarily, these reactants are oxides or minerals expressing the composition of a reactant rock. The reactant names NOMOX are read by CHIM in the

CHIMRUN file, then matched in the MINOX file (see chapter 3). Therefore, the spelling of each reactant (8 characters) must be identical in both the CHIMRUN and MINOX files. If a reactant read in the CHIMRUN file is not matched in the MINOX file, or if a reactant contains a component species that is not specified in the current calculation, an error message results (see chapter 6). If the MINSOLV option is disabled, reactants can still be entered in the CHIMRUN file, but will be ignored. If MINSOLV is non-zero, at least one reactant must be entered in the CHIMRUN file, or an error message will result.

The composition of the reactants (WTPC values) are read in weight percent if MINSOLV is 1 or 2, and are read in mole percent if MINSOLV is 3 or 4. If only one reactant is titrated, then a WTPC value of 100 should be input. The titration increment STEP INCREM is in grams if MINSOLV is 1 or 2; STEP INCREM is in moles if MINSOLV is 3 or 4. TOTAL MIXER indicates the sum of all previous STEP INCREM increments in either in grams or in moles, depending on how MINSOLV is set.

At the start of a reaction calculation, set TOTAL MIXER to zero. For increments in grams, the composition of the system is changed from TOTAL MOLES to TOTAL MOLES + STEP INCREM*WTPC*0.01*spec/mwox, where spec is the molar amount of a given component species in the reactant NOMOX, and mwox is the molecular weight of reactant NOMOX. For increments in moles, TOTAL MOLES are changed to TOTAL MOLES + STEP INCREM*WTPC*0.01*spec. If you desire increments in millimoles or Kilograms or other units, you can always "cheat" by inputing appropriate WTPC values, since WTPC values do not need to sum to one hundred. However, remember that CHIM still considers the increments to be either in grams or moles, and indicates so in the output.

If MINSOLV is 2 or 4, CHIM stops titrating a reactant once it becomes saturated. For this option to work, the spelling of the reactant names in the CHIMRUN and MINOX files must match the spelling of the same phases in the SOLTHERM data file (8 characters). For example if QUARTZ saturates during a granite-water reaction, the reactant QUARTZ in the granite will no longer be titrated. However, if the reactant is specified as SIO2, "SIO2" will not match "QUARTZ" and quartz will continue to be titrated.

At the start of a water-rock titration, TOTAL MIXER and AQGRM should be set to zero. If AQGRM (the weight in grams of the aqueous solution) is zero, CHIM will compute its value for the current solution. From then on, the AQGRM value will not change, and will only be used to compute the water/rock ratio for purposes of the output (see chapter 3).

As for the Coolbrew option (fluid-fluid mixing), all component species contained in the reactants must be specified in the total composition of the system (TOTAL MOLES). If a component species is not present in the chemical system prior to the first titration increment, an TOTAL MOLES value of zero must be entered for that component species in the CHIMRUN file. As discussed above, zero TOTAL MOLES values might create convergence problems, and you might want to set INCREM to 1 for immediate titration of the reactants (skip the TOTAL MIXER = 0 step). Refer to the fluid-fluid mixing section for additional information on this subject.

5.5 Evaporation

Modeling evaporation with CHIM can be accomplished in different ways. The easiest way is to select the fluid-fluid mixing option by setting TEMPC to the current temperature of the solution, and remove water from the system. This can be done by specifying MIXER TOTAL

MOLES(2) to 1 (1 kilogram), and STEP INCREM to a negative value between 0 and -1. Specifying MIXER TOTAL MOLES(2) to -1 and STEP INCREM to a positive value between 0 and 1 will work as well. Naturally, you must make sure that you do not remove more water than the current solution contains, or convergence will fail. When modeling evaporation, you must keep in mind that the reliability of computed activity coefficients is not very good above 3 ionic strength. Evaporating above 5 ionic strength is not recommended.

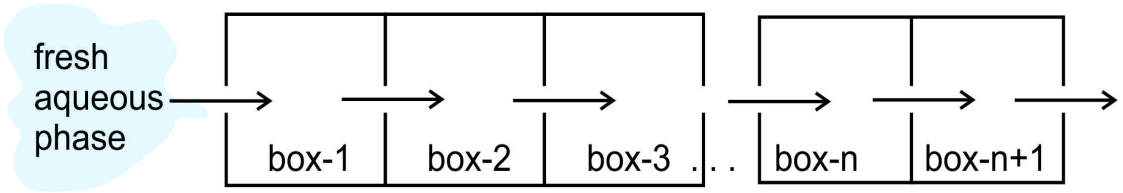
5.6 Oxidation

Oxidation is just one particular type of "mixing" calculation. To oxidize a given system, for example, a rock-water system that is already equilibrated by a rock titration calculation using the Minsolv option, set MIXER TOTAL MOLES's appropriate to one mole of oxygen. At this point, you must recognize whether your starting system is already "oxidized" or "reduced" in its general oxidation state in order to determine whether to specify oxygen as O_2, itself, or in terms of sulfate, etc. (see section 4.3). If the starting solution has a bisulfide concentration in excess of 10^{-30} or so, or $f(O_2)$ less than 10^{-40} at 25 °C, then it is "reduced" and use of bisulfide (SAQ = 6) as a component species (in the CHIMRUN file) is appropriate. In such a reduced case, specify oxygen in MIXER TOTAL MOLES as: -0.5 HS^- + 0.5 SO_4^{2-} + 0.5 H^+. (That is, MIXER TOTAL MOLES(6) = -0.5, MIXER TOTAL MOLES(4) = 0.5, MIXER TOTAL MOLES(1) = 0.5). If the starting solution is oxidized, specify oxygen as O_2 by setting MIXER TOTAL MOLES(31) = 1.0. You cannot mix the use of bisulfide in the TOTAL MOLES's with oxygen in the MIXER TOTAL MOLES's. They are mutually incompatible for expressing composition using the minimum number of thermodynamic components.

To reduce an already oxidized system, specify oxygen as the reactant (in either of the forms outlined above) then use a negative value for STEP INCREM to remove oxygen. Whether oxidizing or reducing, remember that once the calculation reaches the redox "end point" it is common that convergence fails because the value of STEP INCREM is too large to accomodate the very rapidly changing redox state. When convergence fails under these conditions, change STEP INCREM to one tenth of its previous value and continue. Repeating such decimation of STEP INCREM until the redox boundary is crossed, then increase STEP INCREM again. One might also choose to change to the other set of redox species, but such change generally is not necessary to gain convergence. The change over can generally be carried out within a wide zone where either redox component set functions, allowing an overlap in the calculations to verify that all results match. Without exception, we have found excellent matches. Tiny discrepancies (third decimal place) result from the differences in the power functions used to express equilibrium constants as a function of T.

5.7 Box-1 Calculations

Imagine a one-dimensional flow system divided into boxes that contain rock material and some pore space. Fresh aqueous fluid enters at one end into Box-1, equilibrates with the rock,



then moves to box-2, etc. CHIM is equipped to model Box-1 (as before, CHIM also models the leading parcel of fluid with the IFRAC = 1 option). To do a Box-1 calculation:

Set IFRAC = 5

Put the fresh fluid composition in MIXER TOTAL MOLES

Specify the composition of the contents of Box-1 (including pore fluid) in TOTAL MOLES, ordinarily from the end of a previous standard CHIM run using the MINSOLV option.

Specify VOLBOX-1, the volume of the whole of box-1, including minerals and pore space. Usually a good VBOX1 can be determined by setting it to yield a desired porosity in the company of a volume of minerals known from a previous CHIM (MINSOLV option) run.

Specify the density (gr/cm^3) of the fresh fluid, RHOFRESH.

Set STEP INCREM to a value between 0 and 1. STEP INCREM controls the amount of fresh fluid infused into the box-1 pore volume on a given step. The amount replaced is given by STEP INCREM*Gf, where Gf is the number of grams of pore fluid that will fit.

Set SLIM to the limit of the number of units of the MIXER TOTAL MOLES fluid that you wish to put through on a given pick up run. E.g. if SLIM = 5 and the MIXER TOTAL MOLES fluid is specified as 1 kg of pure water, the program will stop after putting 5 kg through box-1.

For box-1 calculation, RHOROC can be zero. It is not used.

5.7.1 Numerical Knots

As with any CHIM run, numerical knots are sometimes encountered. To untie such knots in box-1 calculations, cut the size of STEP INCREM to 0.1 or smaller to step through in small increments (e.g. stepping over a redox cliff). After your are beyond the knot, increase STEP INCREM to 1.0 again.

A sample run file is given below.

```
Titration of quartz-supersaturated water into box-1.
Watch porosity decrease.

<  erpc  ><   ph   >< pfluid ><  temp  ><  tempc ><volbox-1><rhofresh>< rhoroc >
.1000E-11    .00000   1.00000  25.00000            200.     1.0

<     sinc    ><     slim    ><    totmix   >
 1.               5.

<  enth  >< senth  >< denth  >< totwat >< solmin ><   rm   ><  aqgrm >< suprnt >
    .00000    .00000    .00000  90.00000 .0000E+00    .00000 999.90383 .1000E-09

         c ifra ipun nloo iste lims looc ient itre idea ipsa incr incp mins neut
         3    5    2   40    0    1    0    0    0    0    1    0    0    0    0

 saq> < name >    <     mtot     ><     mtry     ><gamma >  <   comtot   >
    1 H+           .000000000E+00  .175422579E-06   .9995   .00000000E+00
    2 H2O          .999899983E+00  .100000000E+01  1.0000   .99989998E+00
    3 Cl-          .934579525E-09  .934670893E-09   .9995   .93457952E-09
    7 SiO2(aq)     .332834074E+01  .100599280E-03  1.0000   .10e-2
   18 Ag+          .934579414E-09  .934670805E-09   .9995   .93457941E-09

< min  >  < mintry >
quartz     .3328E+01

<nomox >  <  wtpc  ><ppm?

<supnam>

<dontfr>
```

5.8 Porosity Calculation

The CHIMRUN file calls for two input values related to computing porosity of a numerical water-rock system. The inputs are "VOLBOX-1" and "RHOROC". VOLBOX-1 was developed originally for box-1 calculations (see above), but it can be used with RHOROC for any rock titration calculation also. Their proper use, however, depends on the user for careful consideration of the goals of the calculation. There are two types of porosity calculation, excluding the box-1 category. Both apply only to MINSOLV-type calculations without fractionation (rock titrated into water at constant T, P; MINSOLV = 1 or 3, ifrac = 0).

a) Type I. The user simply wants to know what volume the product minerals occupy relative to the reactant rock. For example, if a mass (Mr) of reactant granodiorite of density (Dr) reacts with one kilogram of acidic volcanic gas condensate, what volume (Vr) did the reactant occupy relative to the total volume (Vp) of the pyrophyllite, quartz and alunite that replaced it? This type of question arises when examining whether porosity of a rock increases or decreases as a consequence of hydrothermal alteration. If it increases, it enters a positive feedback loop that further enhances reaction. Otherwise, it could shut itself off. Such a loop is explicitly addressed in BOX-1 calculations. A Type I treatment is calculated in CHIM then expressed as a porosity (P) by computing:

$$Vr = Mr/Dr \qquad Vp = \Sigma\, Mk/Dk$$

where *k* refers to the product minerals (e.g. pyrophyllite, alunite, quartz)

$$P = 100\,(Vr-Vp)/Vr$$

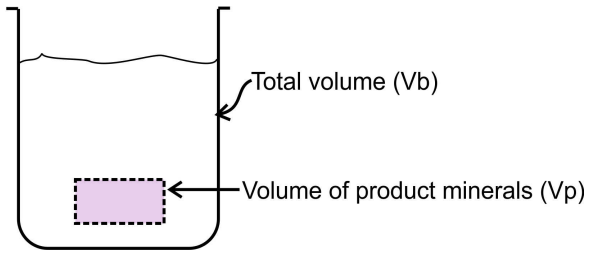
The value of the reactant density, *Dr*, is input as "RHOROC". The product mineral densities, *Dk*, are input in SOLTHERM. To activate this style of porosity calculation, one must set VOLBOX-1 to zero at the outset.

b) Type II. The user wants to know the volume occupied by product minerals relative to the total volume of the initial rock + water system. This arises, for example, when considering diagenesis of a sandstone or conglomerate wherein one is interested in a specific porosity in the rock-water system, e.g. 25%. Since, in MINSOLV-type calculations, rock is titrated into a specific initial mass of liquid, the initial porosity in the rock-water system is 100%; then it decreases steadily from there. At some point in the titration, the porosity is 25%; that is, 25% of the total volume is occupied by minerals.

For a Type II calculation, quantities are computed as for the Type I calculation, above, except the porosity is given by:

$$P = 100\,(Vb-Vp)/Vb$$

where *Vb* is the volume of the total system computed by



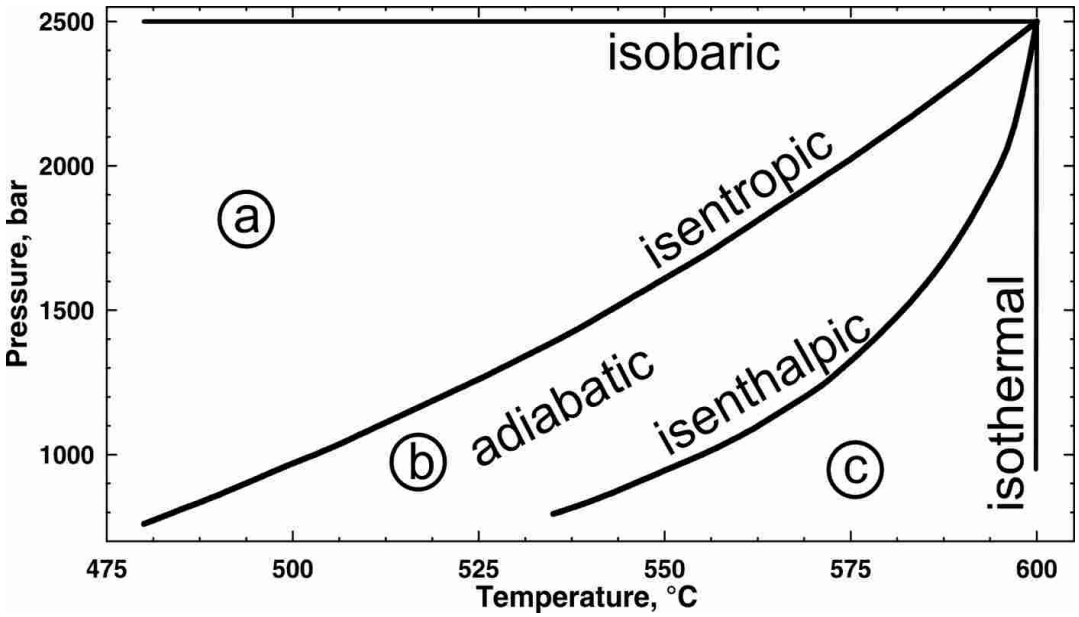
$$Vb = Vb1 + Vr$$

in which *Vb1* is input as VOLBOX-1 (commonly 1000 cm^3 for a kilogram of starting reactant water). Thus on any given titration step, *Vb* is the total of the initial water volume plus the volume occupied by the all of the added rock.

The user must be cognizant of the preceding description of the meaning of "porosity" in the CHIM output. Plan accordingly.

5.9 Temperature-Pressure path calculation

By listing a set of T-P pairs in the CHIMRUN.DAT file under the heading "T-P curve data" the user defines a set of T-P points along which temperature and pressure must change in the course of the calculation. If such point are specified, CHIM will follow that T-P path in a series of equilibrations of whatever composition is specified in the "total moles" column. A common use is to follow an adiabatic decompression path, starting at a chosen pressure and temperature. The hard part about using this option is that the user must define the set of T-P points, thus if one wants a certain adiabatic path, the user must determine the set of T-P points that define that path (e.g. see figure). One caution: Because the current configuration of the logK interpolation scheme (as of August 2010) has some uneven spacing of pressure and temperature values in the P-T grid of logK's, the "edges" where spacing changes yield poor interpolated values, which show up in P-T paths as modest bends in curves. We anticipate correcting this problem soon.



P-T paths for adiabatic decompression from 2500 bar and 600 °C.

6. PROBLEMS AND ERRORS: HELPFUL TIPS

CHIM generally runs easily, and, providing that all input data are in the right shape, problems should be rare. In this chapter, we review the most common problems encountered with CHIM. These problems can be divided into three categories: "clean stops", which are execution stops and error messages built into CHIM, and that are not related to other system errors, "bombs" (execution abortions) related to input/output errors, and "bombs" resulting from convergence problems. Bombs with CHIM can be extremely frustrating. Hovewer, most of these bombs are related to simple problems, such as mistakes in the input data, and are easily corrected. Other more serious bombs relate to numerical problems and machine precision, and might require more effort to solve.

6.1 Clean stops and built-in error messages

All execution stops built into CHIM are accompanied by a message indicating why the execution was aborted. Other error messages do not lead to a program interruption. These messages are reviewed below. Messages are given in the same order as they appear in the program. Routine MAIN indicates the main program.

WARNING! THE NUMBER OF COMPONENTS GIVEN IN CHIMRUN EXCEEDS THE CURRENT ARRAY DIMENSION (__). CHECK CHIMRUN DATA FILE.

From routine: MAIN. Execution stop: YES

Self explanatory. CHIM accepts only up to a certain number of component species (current limit is 50). This message might also occur if there is no blank line after the component species data in the CHIMRUN file.

WARNING! SAQ(__) = ____; MAXIMUM VALUE ALLOWED IS ___

From routine: MAIN. Execution stop: YES

Self explanatory. SAQ values must not exceed the array dimensions specified in CHIM (current limit is 30). Check for format mistakes in the CHIMRUN file, or for an invalid SAQ number.

ABORT. COMPOSITION OVERSPECIFIED. YOU CANNOT USE BOTH O2 AND HS-SIMULTANOUSLY. CHOOSE.

From routine: MAIN. Execution stop: YES

Self explanatory.

TOO MANY SATURATED MINERALS SPECIFIED IN CHIMRUN. LIMIT = ___

From routine: MAIN. Execution stop: YES

Self explanatory. You might have specified too many saturated minerals in the CHIMRUN file, and the matrix dimensions are exceeded (current limit is 40). This message will also occur if there is no blank line after the saturated mineral data in the CHIMRUN file.

TOO MANY REACTANTS SPECIFIED IN CHIMRUN. LIMIT = ___

From routine: MAIN. Execution stop: YES

Self explanatory. There is a limit on the number of reactants that can be specified for a water/gas/rock reaction (current limit is 30). This message will also occur if there is no blank line after the reactant data in the CHIMRUN file.

REACTANT _____ IN MINOX HAS TOO MANY COMPONENTS. ITOT FOR THAT REACTANT IS ___; MAXIMUM IS ___

From routine: MAIN. Execution stop: YES

Dissociation reactions in the MINOX data file are limited to a certain amount of stoichiometric components (current limit is 12). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the MINOX data file (see chapter 3). If ITOT is too large, or improperly aligned, this message will occur.

REACTANT: _____ NOT FOUND IN MINOX DATA FILE.

From routine: MAIN. Execution stop: YES

Self explanatory. Make sure that the spelling of reactants in the CHIMRUN file matches the spelling of the reactants in the MINOX file. If the solid name indicated in this message is blank or is identical to a format indictor (e.g. <supnam>), you probably forgot or misplaced blank lines between the different sections of the CHIMRUN file (see chapter 3). A blank name will also occur in this message if you specify MINSOLV non-zero in the CHIMRUN file, but forget to input a list of REACTANTS in that file.

REACTANT _____ CONTAINS SPECIES NUMBER __ WHICH IS NOT INCLUDED IN THE LIST OF COMPONENT SPECIES FOR THIS RUN.

From routine: MAIN. Execution stop: YES

All species contained in the stoichiometry of a reactant, as read in the MINOX data file, must be input in the list of component species in the CHIMRUN data file. If a component species is absent from the starting solution, but is to be titrated into that starting solution, input a TOTAL MOLES value of zero, or, if a zero value creates convergence problems, input a very small TOTAL MOLES value for that component species. (see chapter 5). The species number in this message refers to SAQ in the CHIMRUN file (see chapter 3).

NUMBER OF SPECIES READ IN SOLTHERM EXCEEDS MAXIMUM OF ___. LAST NAME READ IS:_____ (NS = ___).

From routine: MAIN. Execution stop: YES

The total number of aqueous species read in SOLTHERM cannot exceed the dimension of arrays specified in CHIM. The current limit is 350 species, including the component species. Reduce the number of components in your chemical system, or increase the array dimensions in CHIM. Note that NS in this message should equal the current allowed maximum value.

SPECIES _____ IN SOLTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT SPECIES IS ___; MAXIMUM IS ___

From routine: MAIN. Execution stop: YES

Dissociation reactions in the SOLTHERM data file are limited to a certain amount of stoichiometric components (current limit is 12). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the SOLTHERM data file (see appendix A). If ITOT is too large, or improperly aligned, this message will occur.

NUMBER OF MINERALS READ IN SOLTHERM EXCEEDS MAXIMUM OF ___. LAST NAME READ IS:_____

From routine: MAIN. Execution stop: YES

The total number of minerals read in SOLTHERM cannot exceed the dimension of arrays specified in CHIM. The current limit is a total of 400 minerals and gases (included). Reduce the number of components in your chemical system, or increase the array dimensions in CHIM.

MINERAL _____ IN SOLTHERM HAS TOO MANY COMPONENTS. ITOT FOR THAT MINERAL IS ___; MAXIMUM IS ___

From routine: MAIN. Execution stop: YES

Dissociation reactions in the SOLTHERM data file are limited to a certain amount of stoichiometric components (current limit is 12). The number of stoichiometric components to be read is indicated for each reaction by the integer ITOT in the SOLTHERM data file (see appendix A). If ITOT is too large, or improperly aligned, this message will occur.

_____, SPECIFIED IN CHIMRUN, WAS NOT FOUND IN SOLTHERM. CHECK SPELLING.

From routine: MAIN. Execution stop: YES

Self explanatory. Saturated phases (MINERALS) given in the CHIMRUN file must spell the same as in the SOLTHERM data file. Note that this message will also occur if you include, in the list of saturated phases in the CHIMRUN file, a phase that you also specified as being suppressed from the current calculation.

CHARGE IMBALANCE IN STARTING SOLUTION OR MIXING SOLUTION EXCEEDS GIVEN LIMIT !! CURRENT LIMIT IS: 1.E-4 * TOTAL MOLES OF _____ CHECK INPUT DATA, OR CHANGE C (CHARGE BALANCE ION). IF MIXING, CHECK CHARGE BALANCE OF MIXING SOLUTION. EXECUTION ABORTED.

From routine: MAIN. Execution stop: YES

This message indicates that TOTAL MOLES or MIXER TOTAL MOLES values in the CHIMRUN file are out of charge balance. Adjust charge balance or C ion so that imbalance is less than 10^{-4} x C ion.

END DATA ECHO. SET NLOOP > 0 TO START CALCULATIONS

From routine: MAIN. Execution stop: YES

Self explanatory. This message occurs if NLOOP in the CHIMRUN file is 0.

SIZE OF MATRIX REACHED LIMIT. N = ___. MAXIMUM SIZE IS ___.

From routine: MAIN. Execution stop: YES

Self explanatory. The matrix dimensions cannot exceed the dimensions specified in CHIM (dimensions are N by N, with a current maximum N value of 60). This message will only occur if, during the course of a calculation, too many minerals and/or gases saturate, and the sum of the number of component species plus the number of saturated minerals and gases (plus 1 if enthalpy is used) becomes greater than the allowed limit.

TOO MANY PHASES IN MATRIX (___). MAXIMUM NUMBER ALLOWED IS ___

From routine: MAIN. Execution stop: YES

Self explanatory. See above message. This message occurs if, during the course of a calculation, the number of saturated minerals and/or gases reaches the maximum number allowed (current limit is a total of 40 minerals plus gases). This message does not imply, however, that the matrix has reached its maximum size.

** WARNING ! MOLALITY OF _____ LESS THAN _____

From routine: MAIN. Execution stop: NO

This message is printed if, during the iteration process, the molality of a component species reaches the lowest value allowed by the computer without underflow errors (the current lowest limit is 10^{-300}). Note that convergence will most likely fail if this occurs (even though the ionic strength might converge to a constant value). If this happens with the molality of HS^-, you might have a chemical system that is too oxidized to use sulfide/sulfate as redox species, and you might have to change to using O_2 instead of HS^-.

CHARGE IMBALANCE OF AQ. SOLUTION EXEEDS GIVEN LIMIT. CURRENT LIMIT IS: 1.E-4 * AQ. MOLALITY OF _____ CHECK FOR CONVERGENCE PROBLEMS, OR STOCHIOMETRY ERROR, OR CHARGE IMBALANCE OF MIXING SOLUTION. EXECUTION ABORTED

From routine: MAIN. Execution stop: YES

This message occur after an equilibration calculation has been accomplished, and indicates that the sum of all aqueous species (component and derived) is out of charge balance. It might occur if the calculation never converged and reached the loop limit (see below), if one or more derived species have stoichiometries out of charge balance in SOLTHERM, or if the mixing solution is out of charge balance. If calculations did not converge, determine the reason of non-convergence (see below), otherwise check TOTAL MOLES and MIXER TOTAL MOLES values for charge imbalance. If you have added new species to SOLTHERM, check their stoichiometries.

CHARGE BALANCE OF SOLIDS EXCEEDS 1.E-8. CHECK FOR STOICHIOMETRY

ERROR OF LAST SATURATED MINERAL.

From routine: MAIN. Execution stop: YES

This message occurs if the composition of the saturated minerals and gases, in terms of component species, in exceeds 10^{-8}. Thus, the SOLID MOLES and GAS MOLES column printed on the output must be in charge balance. If not, this indicates that one or more of the saturated solids and gases are "charged", which is impossible, unless the stoichiometry read from the SOLTHERM data file is incorrect.

NUMBER OF ITERATIONS REACHED THE GIVEN LIMIT (___) NON-CONVERGENCE ASSUMED. EXECUTION ABORTED.

From routine: MAIN. Execution stop: YES

If convergence is not reached after NLOOP iterations, CHIM will stop. If the ionic strength values printed on the screen after each iteration seemed to converge, ERPC might have been set too small. 10^{-12} should be the lower limit and should work in most cases. Some cases might require slightly larger ERPC. If that does not do it, then you have a convergence problem. Repeat the calculation with a smaller step. If starting the first run, check all input data and readjust TRIAL MOLALITY (and MIN TRIAL MOLES, if specified) to better estimates.

_____ HAS A TOO LARGE SOLID SOLUTION INDEX (___). MAXIMUM VALUE ALLOWED IS ___.

From routine: SQUOMP. Execution stop: YES

Solid solution indexes (JSOLS in SOLTHERM data file) cannot exceed the dimensions specified in CHIM (current limit is 20).

_____ IS PART OF A SOLID SOLUTION WITH TOO MANY END MEMBERS (___). MAXIMUM NUMBER ALLOWED IS ___.

From routine: SQUOMP. Execution stop: YES

A solid solution cannot have more than a maximum number of end members (current maximum number of end members allowed for each solid solution, or mixed gas phase, is 20).

TEMPERATURE REACHED GIVEN LIMIT OF _____ TEMP = _____ EXECUTION STOPPED.

MIXING FRACTION REACHED UPPER LIMIT OF _____ TOTAL MIXER= _____ EXECUTION STOPPED.

PRESSURE REACHED GIVEN LIMIT OF _____ PFLUID = _____ EXECUTION STOPPED.

ENTHALPY REACHED GIVEN LIMIT OF _____ ENTH = _____ EXECUTION STOPPED.

From routine: COOLER. Execution stop: YES

These messages will occur at the end of a calculation step, if the next step is past the limit given by TLIM. Set TLIM to a higher or lower limit to continue the calculations.

WARNING, MOLECULAR WEIGHT OF REACTANT _____ IS 0. CHECK MINOX DATA FILE FOR ERRORS OR DOUBLE ENTRIES.

From routine: BULK. Execution stop: YES

Self explanatory. Remember that the MINOX data file cannot have two phases with identical names.

CHARGE IMBALANCE OF REACTANTS IN MINOX EXCEEDS 1.E-8. IMBALANCE = _____; CHECK FOR STOICHIOMETRY ERROR IN MINOX. EXECUTION ABORTED.

From routine: BULK. Execution stop: YES

Self explanatory. Like in the SOLTHERM data file, the stoichiometries of reactants in the MINOX data file must be in charge balance. This message might also occur if the amounts of reactants specified in the CHIMRUN file (WEIGHT PERCENT) are improperly specified or aligned.

******** WARNING ******** COMPUTATIONAL SINGULARITY, IV(N) = 0.0

From routine: SIR. Execution stop: YES

This message is printed in case computational singularity occurs. This will occur if the system is overdetermined (e.g. if a component species can be expressed in terms of other component species, or if two component species, or two minerals in matrix are similar). This message usually arise if gypsum is part of the equilibrium assemblage and anhydrite supersaturates, or vice versa, because there is only one single activity of water at which both can co-exist. It might also occur if the equilibrium assemblage is such that it violates the phase rule, e.g. if both quartz and cristobalite are specified as saturated minerals, or if the number of phases exceeds the number of components for a sub-system of the whole system. Check to see if, by mistake, similar minerals are specified, or if one or more component species repeat in CHIMRUN. You might also restart the calculation with a smaller step increment. If the error occurred after CHIM added a new mineral in the matrix, determine what this new mineral was. Use common sense and guess which mineral(s) (already in matrix) this mineral might be replacing. Use the CHIMRUN .SAV file (device IOUT3) as pickup file and swap minerals by hand. Run CHIM again with the new given mineral assemblage and see if it makes it. If it does not, try another swap, and so on. Generally, the correct swap is easily determined (e.g. gypsum for anhydrite, hematite for pyrite, etc). If this error occurs after consecutive "bombs" and system errors, it might also be related to computing difficulties (see below, and convergence problems section).

********** WARNING **********
THE SYSTEM IS ILL-CONDITIONNED

From routine: SIR. Execution stop: NO

This message indicates computational difficulties and is often accompanied by system error messages, if not by a "bomb". Try a smaller step increment, or hand swapping of minerals as described above. See also convergence problems section.

6.2 Input/Output errors

In this section, the most common input/output system errors are reviewed. Numerical problems are discussed in the convergence "bombs" section below.

- END OF RECORD ERRORS

These errors are rare when running CHIM on microcomputers. If they occur in when executing CHIM on a main frame, re-examine the file assignments that are made external to CHIM. The best way is to incorporate the assignments into a command file. Check all file assignments and input file record lengths. Make sure that CHIMRUN file is within format specifications. The SOLTHERM data file needs two blank lines at the bottom of the mineral data. Check for enough disk space for output files.

- ILLEGAL DECIMAL CHARACTERS

This will happen anytime CHIM reads something that it is not expected to read. Check all input file formats. The SOLTHERM data file needs two blank lines after the component species, after the derived species data and after the mineral data. The input file CHIMRUN needs blank lines and format indicator records between the different sections (see chapter 3).

6.3 Convergence problems

Welcome to the most frustrating part of numerical modeling! Unfortunately, numerical modeling of some chemical systems can be tedious because of numerical difficulties. Convergence problems are generally worse for systems with a large number of component species and many saturated minerals (and gases), and solid solutions among the saturated minerals. A convergence problem will cause CHIM to reach the given loop limit (NLOOP) without converging, or to "bomb" before that limit is reached. In the past when executing on mainframes, convergence "bombs" arose from OVERFLOWS and UNDERFLOWS, but these should be rare these days.

If you encounter convergence problems, the first thing to do is to check that all the previously discussed problems are taken care off (this will take care of 90% of the problems). Beyond this, the overwhelming majority of convergence problems relate to phase selection conflicts (often involving solid solutions) that CHIM is not programmed to resolve but which the user can readily identify and correct (with practice).

If starting an original run, convergence problems generally result from poor guesses for TRIAL MOLALITY and MIN TRIAL MOLES values. If too many "wrong" minerals are given in CHIMRUN (MINERAL names), CHIM will quickly diverge. Check on an output (setting NLOOP = 0) that all minerals given in CHIMRUN have a non-zero amount equal to MINERAL TRIAL MOLES in the TRIAL MOLES column, and that all other minerals have zero amounts. Convergence problems might also be related to a wrong selection of parameters, depending of

the type of calculation selected (cooling, boiling, or mixing), although CHIM should identify such problems and rectify them in most cases.

Most convergence problems occur after a step increment has been accomplished. The first thing to try in such cases is to restart the calculation from the last equilibrated run with a smaller increment step (STEP INCREM), e.g one tenth of the previous STEP INCREM. If this does not help, or if the step has to be reduced to smaller and smaller values in order for the calculation to creep ahead slowly, there might be a numerical problem, or "knot". An example of such problem could happen when titrating an oxygenated solution into a reduced solution containing a lot of iron. The first titration increment, for example, might require hematite to saturate, no matter how small the increment is. With the current component species in SOLTHERM, titrating an oxygenated solution corresponds to titrating, among other species, a negative amount of sulfide and a positive amount of sulfate. CHIM might encounter numerical difficulties in equilibrating a solution with a negative amount of sulfide, without having a saturated mineral, like hematite, accounting for the negative sulfide amount. To solve this problem, you can input hematite by hand in CHIMRUN, and run CHIM with INCREM set to 1, which will cause the program to first titrate, before equilibrating.

Another similar problem might occur if, from one step to the next, a phase has to undersaturate (typically a solid solution, see chapter 4) or replace another one, and numerical difficulties are encountered during the computations from one equilibrium assemblage to the other. In such cases, the user can guess the mineral assemblage for the next step and input it in CHIMRUN, and CHIM can then be run with INCREM set to 1 (see also computational singularity and ill-defined system errors in this chapter). Undersaturating solid solutions cause convergence problems if LIMSOL is not set to 2, and, in a few rare cases, might still cause problems during the first five iterations even if if LIMSOL is set to 2. If one or more end-members of a saturated solid solution are present in very small amounts (e.g. $<10^{-15}$), and LIMSOL is not set to 2, convergence problems might occur. Setting LIMSOL to 2 will cause CHIM to throw out the insignificant end-members and reach convergence. However, the LIMSOL = 2 option has its disadvantages, as described in chapter 3. If solid solutions cause too many problems, you might want to suppress them altogether by setting LIMSOL to 0, or you might "break" a specific solid solution by setting JSOLS to 0 in SOLTHERM (see appendix A). This will cause CHIM to treat each end-member as a single phase. Note that if you remove an endmember from the CHIMRUN file, CHIM will only consider the endmembers remaining in the CHIMRUN file as part of the solid solution.

Rarely, convergence problems relate to the composition of the aqueous phase. CHIM brackets all molalities of derived species between 10^{-300} and 10, to avoid over- and underflow problems. If you are executing a CHIM version using a compiler that does not allow numbers as small as 1.e-300 (e.g. old typical minimum was 1.e-70) you may encounter problems when the molality of a component species becomes very small. The best example of such a problem is running CHIM with an oxygenated solution. Redox in SOLTHERM is expressed in terms of HS^- and SO_4^{2-}. The speciation calculation with an oxygenated solution will yield a value for the molality of HS^- that is so small (well below 10-70), that most computers will not be able to handle it. In such case, the choice of component species can be changed by selecting O2 instead of HS- in the CHIMRUN file, thereby causing CHIM to select the set of reactions from SOLTHERM that express equilibria in terms of O_2 instead of HS^-. This arrangement allows one to run CHIM in very oxygenated systems without convergence problems.

If the ideas above do not help with your problems, and you are now experiencing the most frustrating moments in your existence, do not give up. There are two more possibilities that might resolve your problem(s). If convergence is not reached, but there are no obvious reasons as for why, there might be numerical difficulites with the Newton-Raphson convergence process itself. There are two options in CHIM to improve convergence, RM, and ITREF. ITREF will generally not help unless there are precision limit problems with the computer. This should not the be the case with most computers if double precision is used. See chapter 3 for discussion of how to turn on ITREF.

The RM option tries to force convergence by decreasing residuals after each iteration. The way to use the RM option is to first run CHIM with RM = 0.9. If that does not do it, try again with 0.8, 0.7, etc. This option might cause divergence if used with a system that normally converges. In any case, ITREF and RM should be last resort options. If these options do not help, you might have reached a numerical impossibility, or you might be dealing with an impossible chemical system. Defeat is hard to take, but you will have to accept the harsh facts of reality, and modify the calculations scheme, or the chemical system you are dealing with.

7. MINTAB

Program MINTAB is used to read plot files from CHIM or GASWORKS, or the main output file from SOLVEQ then generates an ASCII file with selected data in tabular (columns) format for input into commercial plotting packages. MINTAB reads an unlimited number of datasets in the CHIM, GASWORKS, or SOLVEQ output files. No maximum number of datasets is imposed because MINTAB does not store all the plot data in memory (the size of the plot file to read is limited only by the amount of disk storage).

7.1 How to use MINTAB-XPT on output from CHIM-XPT and GASWORKS

MINTAB-XPT ("MINTAB", for short, herein) is a FORTRAN program that reads plot files from programs CHIM (CHIMPLOT.DAT) and GASWORKS (WORKPLT.DAT) and produces an ASCII file with selected data in tabular format. MINTAB is quite interactive -- asking the user to specify what to plot and what style of plotting to use. The type of data to output in tabular format (i.e. temperature, pressure, etc.) can be specified interactively or (better) by a list of command strings entered in an ASCII file (MINTAB.PAR). This file can be created with a text editor or by running MINTAB. The default name for this file is MINTAB.PAR but any other file name can be specified.

7.1.1 Description of CHIM-XPT and GASWORKS Plot Files

Each time CHIM-XPT (or GASWORKS) is run, a file named CHIMPLOT.DAT (or WORKPLT.DAT) is created. Usually, a complete numerical model run requires five, ten, or fifty run segments (pickups) to produce a final result. Each run segment creates a plot file named CHIMPLOT.DAT (or WORKPLT.DAT). For each run segment, the file CHIMPLOT.DAT (WORKPLT.DAT) must be saved by the user and given a new name. The naming convention that seems to be the most convenient is

AAAANPLT.MMM

where

AAAA = a four letter abbreviation to identify the calculation
N = the calculation number to distinguish one of a series of related calculations
PLT = identifies a plot file, as distinct from an input or output file
MMM = the alpha-numeric sequence number of a particular run segment

Typical file names are: ACID1PLT.D02, RED5PLT.D15, YLST3PLT.D10.

For a run containing ten segments, one might have the following set of plot files: ACID5PLT.D01, ACID5PLT.D02, ..., ACID5PLT.D10. However, any other naming convention that you find convenient can be used.

7.1.2 How to Prepare CHIM-XPT and GASWORKS Plot Files for program MINTAB

The following steps explain how to prepare the plot files produced by CHIM-XPT and GASWORKS for use with MINTAB.

1) The separate run segment plot files must be concatenated into one file using the DOS "copy" command. The segments must be in the order they were created. For example, if the following segments were created

ACID1PLT.D01
ACID1PLT.D02
ACID1PLT.D03

they would need to be placed in a file in the order D01, D02, D03, then the DOS copy command would be applied at the command prompt:
copy ACID1PLT.D0* ACID1PLT.SUM to produce the concatonated file ACID1PLT.SUM, to be read by MINTAB. Below, the sum file is called AAANplt.SUM.

2) Copy the AAAANplt.SUM and any one output file segment to the sub-directory which contains MINTAB, or vice versa. Output files are created by CHIM-XPT and GASWORKS with the default names of CHIMOUT.DAT and WORKOUT.DAT, respectively. For them ,it is convenient to use the same basic naming convention described above, e.g. AAAANout.MMM.

7.1.3 Using MINTAB

1) To run MINTAB, type MINTAB-XPT at the command prompt.

2) MINTAB asks for the type of data to be read: (1) chim-xpt plot file, (2) gasworks plot file, (3) solveq output file. Enter (1).

3) Next, MINTAB prompts for the name of the file to be processed (default = CHIMPLOT.DAT). This is the AAAANplt.sum or "SUM" file. If this file is not in the current directory, the program will keep prompting until a valid filename is entered or until the user aborts the program using control-break or control-C.

4) If MINTAB has not previously created a label file for this calculation, it prompts for the name of an output file (default = CHIMOUT.DAT) segment from which it will read the names of all aqueous species used in the calculation, and then creates the label file AAAANplt.lab (default = CHIMPLOT.lab).

5) MINTAB prompts for the name of the file in which the results will be tabulated (default = CHIMPLOT.tab).

6) MINTAB asks if the user would like to use an existing parameter plot file (default = yes).
a) If yes press [enter]. MINTAB will then prompt for the name of that file (default = mintab.par). Enter the file name if it is not the default name. MINTAB will complete execution with no further input.
b) Enter 'n' to create a new one.

7) MINTAB will present a list of general parameters to be tabulate:

```
1 = Temp              5 = Tempc
2 = Pfluid            6 = Enthalpy
3 = pH                7 = Porosity
4 = Mix.frac          8 = Gas_wt.%
```

Select the parameters you wish to tabulate by typing the integer indices separated by commas or spaces.

8) MINTAB will present a list of other parameters to tabulate:

```
1 = Individual species molalities
2 = Total moles of components
3 = Total aqueous moles component species
4 = Log Fugacities of gases
5 = Minerals
```

Select one integer index.

9)

a) Except for option 5 in step 8) above, minerals, MINTAB will then present a list of items for the option selected. Select the parameters you wish to tabulate by typing the integer indices separated by commas or spaces.

b) If option 5 in step 8) above, minerals, is selected, MINTAB will present a list of available mineral data:

```
1 = Moles
2 = Grams
3 = %
4 = Mole Fraction
```

Select one integer parameter. MINTAB will then present a list of minerals and gases. Select the minerals you wish to tabulate by typing their integer indices separated by commas or spaces. MINTAB will then ask:

```
Which minerals do you want to divide, if any
input mineral index and dividing factor (e.g. 6,5.0)
```

Enter the parameters as directed, or press [enter] only to skip this step.

10) MINTAB will then ask:

```
Do you want to tabulate more data ? (default=yes) :> n
```

If yes, press [enter] and MINTAB will return to step 7, above. If no, enter ‘n’.

11) MINTAB will then ask:

```
Enter name of parameter file to create
(default = mintab.par  ) :>
```

Enter the file name, or press [enter] only to use the default. If the file already exists MINTAB will ask whether to replace it. If user answers no, MINTAB will ask for another file name; enter this name. MINTAB will then complete execution.

APPENDICES

A: MORE ABOUT THE SOLTHERM DATA FILE

The SOLTHERM file contains all thermodynamic data for aqueous, gas, and mineral species. This file generally does not have to be modified by the user. SOLTEHRM is divided into eight parts: the comment area, the activity coefficients data, the water enthalpy data, the component species data, the derived species data (aqueous), the gas data, the mineral data, and optional miscellaneous data.

The Comment Area

The comment area is skipped by CHIM, and can be of any length. It contains various comments and references for the thermodynamic data. If you are planning to modify this file, the user should read and understand all the comments. Some of the content of the comment area is repeated here. Whenever updating SOLTHERM, it is important to make a note in the comment area concerning the changes or updates. This area is delimited at the bottom by a record with at least 8 stars in the first 8 columns:

* Last record of comment area: ******** (eight *'s or more)

The Activity Coefficients Data

These data are used by CHIM to interpolate activity coefficients of charged species. This area contains 156 records, 39 records for each of four Debye-Huckel parameters, ADH, BDH, BINACL and BIL from Helgeson et al. 1981. The first record for each parameter is blank, and the second record is not read by CHIM. The next 37 records each contain 36 real values. The 37 records correspond to the following 37 pressures in bar:

```
1.000, 1.0133, 2.321, 4.758, 8.919, 15.537, 25.479, 39.737, 59.432,
85.839, 120.458, 165.212 (liquid-vapor saturation)
200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850,
900, 950, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, 5000
```

The 36 real values in each record correspond to the following temperatures in °C:

```
0.01,  25,  50,  75, 100, 125, 150, 175, 200, 225, 250, 275, 300,
325, 350, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500,
510, 520, 530, 540, 550, 560, 570, 580, 590, 600
```

These records are Fortran "free format" meaning the alignment of the real values requires only that they be separated by a comma or blank space. Where values equal 99999.999, absence of data is indicated. Data are absent where the density of water is less than 0.35 g/cm^3 **This scheme of 37 records with 36 values in each is also used for water enthalpy and log K data for derived species, minerals and gases.**

Water Enthalpy Data

These data are used by CHIM to compute the final temperature when mixing two fluids of different temperature. This area contains 39 records. The first record for each parameter is blank,

and the second record is not read by CHIM. The next 37 records or 36 real values contain water enthalpy in kJ/mole using the same T, P scheme described above for activity coefficients.

The Component Species Data

These data immediately follow the water enthalpy records described in the previous section, and consist of one record per component species, as follows.

* Each record (A20, F2.0, 6X, F3.2,8x, 3F8.4): AQS_NAME, CHG, AZERO, W, ALKALINITY

For each component species, AQS_NAME is the name, CHG the charge, AZERO the effective ionic radius (Helgeson et al. 1981), W the molecular weight, and ALKALINITY protonation coefficient for alkalinity calculations (this last parameter is only used by SOLVEQ-XPT).

The order of these records should not be changed. For the stoichiometries of derived species, gases, and minerals described in the next sections, each component species is identified by its position in the component species data area (H^+ is 1, H_2O is 2, SiO_2 is 7, etc), and the order of component species in this area is critical. The total number of component species in SOLTHERM may vary, but must be consistent with the array dimensions specified in the programs reading this file.

* Last record must be blank.

The Derived Species Data

This area contains data for aqueous derived species, and follows the component species data area, preceded by one blank line. The data for each derived species is given by 3 records, which are the following:

* 1st record (A20,T81,A4,T91,A4): AQS_NAME, SUP, PTFLAG_AQS

AQS_NAME is the same as for the component species. SUP: any non-blank character read by SUP in columns 81-84 suppresses the species from the calculations.

Derived species, mineral and gas log K data are of two types. The log K data either covers the entire range from 0.01-600 °C, 1-5000 bar, or it is restricted to T and P conditions of liquid-vapor saturation from 25-350 °C (see below). PTFLAG_AQS is a four character string to indicate to the software which type of log K data will be read: "All " indicates the entire range, and any other string indicates the restricted range. If the CHIMRUN file integer parameter L/V-HiP: is set to one for high pressure calculations, log K data that are restricted to liquid-vapor saturation are skipped.

* 2nd record (8X,F3.0,15X,F5.2,10X,F6.3): CHG, AZERO, ALKALINITY

CHG, AZERO and ALKALINITY are the same as for the component species. The end of this record also indicates a reference code for the data, with the exact reference given in the comment area.

* 3rd record (I2,1X,12(F10.3,I2): ITOT, COEF(i) and SPEC(i) where i = 1 to ITOT

ITOT is the number of component species in the derived species. COEF(i) contains the stoichiometric coefficient for species SPEC(i) in the derived species. SPEC(i) identifies the component species in the derived species, and correspond to the position of component species in

the component species area (e.g. SPEC = 1 for H^+, 7 for SiO_2, etc.). If a derived species contains H^+, H^+ MUST be entered in the i = 1 position.

* 4th to 40th, or 4th record only (free format; each real value separated by one comma and/or at least one blank space): LOG K's

The records that follow contain log K data: either (1) 37 records with 36 values each where data are available for the entire T, P grid using the same arrangement as described above for activity coefficients, or (2) a single record for species where data are restricted to conditions of liquid-vapor saturation. In the latter case log K values are typically given for the following temperatures: 25, 50, 100, 150, 200, 250, 300 C, and 350 °C, but in some cases are restricted to a maximum temperature lower than 350 °C; CHIM-XPT will warn the user in the CHIMOUT file if T specified in the CHIMRUN is above the range given for that derived species, and it can then be suppressed from the calculations.

* Last record: must be BLANK.

The total number of derived species in SOLTHERM may vary, but must be consistent with the array dimensions specified in the program. To insure proper reading of SOLTHERM, a extra blank line has to be inserted after the data for the last derived species:

The Gas Data

The first 10 records of this area contain data for computing fugacity coefficients and enthalpies of H_2O-CO_2-CH_4 mixtures:

* First 10 records (A8,6E12.5)

These records contain regression coefficients a, b, and c to calculate cross-virial coefficients B_{ij} and C_{ijk} as a function of temperature (for a virial equation in pressure), such that B_{ij} or $C_{ijk} = a/T^2 + b/T + c$, with T in K (Spycher and Reed, 1988). For the names in these records (e.g. B12, C123) the numbers 1, 2, and 3 correspond to H_2O, CO_2, and CH_4, respectively. This block is followed by two blank records.

The next records contain data for gases. H_2O, CO_2, and CH_4 must always be the first 3 gases, in this order, in the gas list. The data for each gas are given by 4 records, as follows:

* 1st record (A20, T67,I2,F8.3,T81,A4,T91,A4): MIN_NAME, JSOLS, B, SUP, PTFLAG_MIN

MIN_NAME is the name of gas or mineral species. MIN_NAME for H_2O, CO_2, and CH_4 must always be: "H2O, gas", "CO2,gas", and "CH4,gas" followed by 13 blanks for a total of 20 characters. Following MIN_NAME beginning in column 21 is and alternate descriptor of the gas that is not read by CHIM. JSOLS and B are non-zero for gases and mineral solid solutions (see mineral data section). For gases, B is useless, but must always be 1, and JSOLS identifies the species as being a gas species, and must always be 6. If JSOLS is zero for one or more gases, these gases will be treated as minerals, and will not be included in the gas phase if boiling occurs. Gases with JSOLS = 0 do not have a fourth entry, and must be placed after the list of gases which have JSOLS = 6. SUP performs a similar role as for derived species: any non-blank character read by SUP in columns 81-84 suppresses the species from the calculations. PTFLAG_MIN performs the same role as PTFLAG_AQS does for derived species. PTFLAG_MIN is a four

character string to indicate to the software which type of log K data will be read: "All " indicates the full T-P grid, and any other string indicates the range restricted to conditions of liquid-vapor saturation. If the CHIMRUN file integer parameter L/V-HiP: is set to one for high pressure calculations, log K data that are restricted to liquid-vapor saturation are skipped.

* 2nd record (T14,F8.3,T59,F6.3): XMOLW
XMOLW is the molecular weight. The end of this record also indicates a reference code for the data, with the exact reference given in the comment area.

* 3rd record (I3,12(F9.3,I3)) ITOT, COEFM(i) and SPECM(i) i = 1 to ITOT
The 3rd records for gases are similar to the 3rd records for derived species (see derived species section).

* 4th record, only if JSOLS = 6 (4x,6f12.5):
This record contains regression coefficients a, b, c, d, e, and f to calculate virial coefficients B and C of pure gases as a function of temperature (for a virial equation in pressure), such that B = a/T2 + b/T + c, and C = d/T2 + e/T + f, with T in K (Spycher and Reed, 1988). For gases with JSOLS = 0, this record must be omitted. For gases with no data available, this record is left blank and ideal gas behavior is assumed.

The total number of gases in SOLTHERM may vary, but must be consistent with the array dimensions specified in the program. Currently in CHIM, up to 20 gases can be included in the gas phase. If required, additional gases can be added to the mineral data section (see below), but these gases must then have JSOLS set to zero. Generally, O2 and other gases with very low fugacities have JSOLS set to zero, and are not included in the gas phase in boiling calculations. This is to avoid possible underflow and overflow problems.

* 4th to 40th, or 4th record only. If JSOLS =6 5th to 50th, or 5th record only (free format; each real value separated by one comma and/or at least one blank space): LOG K's
These records for gases are similar to the 3rd records for derived species (see derived species section).

The Mineral Data

The data for minerals immediately follows the gas data. The data for each mineral are given by 3 records, which are identical to the 1st, 2nd and 3rd records for gases (see previous section), except that the SUP parameter in the 1st record must be blank. If SUP is not blank or "GAS " (for gas species), the mineral is suppressed from the calculation. Also, the 2nd record contains two more variables, the mineral molar volume (not read by CHIM), and the mineral density, in g/cm^3 for volume calculations. If no density is given, CHIM assigns a density of 2.5.

* 1st record (A20, T67,I2,F8.3,T81,A4,T91,A4)
* 2nd record (T14,F8.3,T59,F6.3)
* 3rd record (I3,12(F9.3,I3))

For mineral solid solutions, B represent the exponent for mineral end-member to be used to calculate activity using ideal multi-site mixing, and JSOLS identifies the index of the solid

solution (if any) to which this mineral belongs. See the comment area in SOLTHERM to check the current solid solutions and their JSOLS indexes. JSOLS = 6 is reserved for gases, and JSOLS = 10 is reseved for electrum.

The total number of solid solutions and of their end- members must be consistent with the array dimensions specified in the program. The total number of minerals in SOLTHERM may vary, but must also be consistent with array dimmensions. To insure proper reading of SOLTHERM, two blank lines have to be inserted after the data for the last mineral:

* Last two records: must be BLANK.

Optional Miscellaneous Data

This area is not read, and can be used to save various data. It is useful for saving records of SOLTHERM that are not presently used, but that might be needed at some further time.

B: MORE ABOUT THE CHIMPLOT DATA FILE

This file contains a condensed version of the calculation results to be used for plotting with program MINTAB. If the "ipun" parameter has been properly set to "1" for the very first run segment, the CHIMPLOT file will contain a first line with the species counts, followed second and third lines with the same title lines as CHIMRUN. (MINTAB bombs are commonly a consequence of these lines being missing.) Immediately following the three header lines, the calculation results are tabulated. Two blank lines must follow the data set for each calculation step. The CHIMPLOT file contains the following records:

* Record 1 (16I5) BSTOT, NST, ITGAS

BSTOT is the total number of component species in this run. NST is the total number of aqueous species (component + derived). ITGAS is the total number of gas species whose fugacities are tabulated.

* Record 2 (10A8) TITLE1
* Record 3 (10A8) TITLE2

TITLE1 and TITLE2 contains two lines of run title copied from CHIMRUN.

* Record 4 (2F10.5,E10.4,2F10.5): temperature, pressure, activity of H+, TOTAL MIXER, and TEMPC.

* Next record(s) (8E10.4): MTRY(i) i = 1 to NST

These records contain the molalities of each individual aqueous species. The number of records depends on how many (NST) aqueous species are included in the calculation (8 species per record).

* Next record(s) (8E10.4): TOTAL MOLES(i) i = 1 to BSTOT

These records contain the total molalities of each component species. The number of records depends on how many (BSTOT) component species are included in the calculation (8 species per record).

* Next record(s) (8E10.4): AQM(i) i = 1 to BSTOT

These records contain the total molalities of each component species in the aqueous phase only. The number of records depends on how many (BSTOT) component species are included in the calculation (8 species per record).

* Next record(s) (I3,2X,A8,2X,F10.5): gas index, name, and log fugacity.

The number of records depends on how many gases (NGAS) are included in the calculation (1 gas per record). These record are only output for gases with JSOLS = 6 (see SOLTHERM section). If gases are saturated, the data in these records become useless, and relevant gas data will appear with the saturated phase data below.

* Next record(s) (I3,2X,A8,2X,7E10.5): saturated phase index, name, moles, grams, weight percent, and mole fraction of end-member if part of a solid solution or gas phase.

The number of records depends on how many phase are saturated in the current calculation

step (1 record per phase).

* Next 2 records: MUST BE BLANK, and indicate the end of the data set for the current equilibration step.

The data set for the next equilibation step follows, and has a format identical to the format described above. Program MINTAB reads data sets limited in number only by hard disk capacity.

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EXAMPLE CHIM APPLICATIONS

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