TOUGHREACT V3.32 Reference Manual:
A Parallel Simulation Program for Non-Isothermal Multiphase Geochemical Reactive Transport

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1   Introduction

This reference manual for TOUGHREACT V3.32-OMP describes in detail the code options and governing equations for reactive transport as well as revisions to the core TOUGH2 heat and fluid flow parameters and capabilities. In addition to this manual, it is necessary to have the TOUGH2 V2 manual. In prior versions of TOUGHREACT, the User's Guide included a set of Sample Problems with relevant inputs, outputs and conceptual model descriptions. For ease of use, these sample problems have been updated for V3.0-OMP and are described in the separate document "TOUGHREACT_V3-OMP_SampleProblems.pdf". Because there are many options which are used frequently, a new addition to the documentation is a concise description of the main inputs in "TOUGHREACT_V332_QuickRef.pdf".

Coupled modeling of subsurface multiphase fluid and heat flow, solute transport, and chemical reactions can be applied to many geologic systems and environmental problems, including diagenetic and weathering processes, geological carbon storage, subsurface nuclear waste emplacement, geothermal systems, acid mine drainage remediation, contaminant transport, and groundwater quality. To investigate these and other problems, TOUGHREACT has been developed by introducing reactive transport into the existing framework of a non-isothermal multi-component fluid and heat flow simulator TOUGH2 (Pruess et al., 1999). A number of subsurface thermo-physical-chemical processes are considered under various thermohydrological and geochemical conditions of pressure, temperature, water saturation, and ionic strength. TOUGHREACT can be applied to one-, two- or three-dimensional porous and fractured media with physical and chemical heterogeneity. The code can accommodate any number of chemical species present in liquid, gas and solid phases.

The first version of the TOUGHREACT code was released to the public through the US Department of Energy's Energy Science and Technology Software Center (ESTSC) in August 2004. It was one the most frequently requested of ESTSC's codes. The code has been widely used for studies in CO_2 geological sequestration, geothermal energy development, nuclear waste isolation, environmental remediation, and for petroleum exploration applications. Over the last several years, many new capabilities have been developed within different research projects at Lawrence Berkeley National Laboratory. To effectively serve our in-house projects and to share with the user community, new capabilities were added to TOUGHREACT V2 and V3-OMP which are distributed through LBNL Tech Transfer. This document describes the features of TOUGHREACT V3.0-OMP.

Version 3.0-OMP adds the following major capabilities and improvements to V2:

- OpenMP parallelization of chemical and coupling routines for much faster performance on multi-core shared memory computers.

- Composition and temperature-dependent mineral heat capacities dynamically updated
- Composition and temperature-dependent mineral thermal conductivities dynamically updated
- Temperature-dependent bulk-rock heat capacities
- Temperature-dependent bulk-rock thermal conductivities
- Heats of reaction calculated from thermodynamic data coupled to energy conservation (heat transport) equation
- Option to fix specified gas species fugacities
- Transport of trace gas species in CO_2-H_2O carrier gas (EOS2 & ECO2n)
- Option to inject trace gas species and assign gas injection zones
- Consistent use of gas properties using calculated densities rather than ideal gas law
- Option to recalculate reactive surface areas within chemical iterations
- Improved flow and reaction coupling for ECO2n and EOS2 (water and CO_2 from reactions)
- New single (aqueous) phase nonisothermal wellbore flow model with wellbore output file
- Options for Leverett-scaling of capillary pressures in fractured and multiple-continua media
- Read and write meshes up to 999,999 grid blocks instead of <100,000
- Improvements in permeability-porosity coupling and tracking through restarts
- Improvements and bug fixes for chemical convergence, efficiency, and accuracy
- Improvements and new options for inputs and outputs

Major additions and improvements in Version 2 included:

- Intra-aqueous reaction kinetics and biodegradation
- Surface complexation models
- Multi-site exchange
- Improvements on the reactive surface area algorithm for mineral-water reactions, and fugacity coefficient corrections for gas-water reactions
- Improvements on coupling between chemistry and physics (such as with porosity and permeability changes)
- Improvement on the ideal mineral solid-solution model
- Improvement on functionalities such as printout of mineral reaction rates, and output of aqueous and surface complexes concentrations with time
- More flexible input formats for chemical parameters
- Significant increase in computational efficiency

TOUGHREACT has been applied to a wide variety of problems, some of which are included as examples in this manual, such as:

- Supergene copper enrichment (Xu et al., 2001)
- Coupled thermal, hydrological, and chemical processes for nuclear waste disposal (Xu et al., 2001; Sonnenthal et al., 2003, 2005; Spycher et al., 2003a, b; Dobson et al., 2003; Mukhopadhyay et al., 2009)
- Mineral alteration in hydrothermal and geothermal systems (Xu and Pruess, 2001a; Xu et al., 2004a and 2006; Dobson et al., 2004; Todaka et al., 2004; Xu et al., 2009a, Wanner et al., 2014)
- Mineral trapping for CO_2 disposal in deep saline aquifers and basaltic rocks (Audigane et al., 2007; Gherardi et al., 2007; Xu et al., 2004b, 2006, 2007; Zhang et al., 2009, Aradottir et al., 2012, 2013)
- Reactive transport and biogeochemical nitrogen cycling in vadose zone systems (Singleton et al., 2004; Xu, 2008; Gu et al., 2008, Maggi et al., 2008)

The TOUGHREACT program makes use of "self-documenting" features. It is distributed with a number of input data files for sample problems. Besides providing benchmarks for proper code installation, these can serve as a self-teaching tutorial in the use of TOUGHREACT, and they provide templates to help jump-start new applications. The fluid and heat flow part of TOUGHREACT is derived from TOUGH2 V2, so in addition to the current manual, users will need the manual of TOUGH2 V2 (Pruess et al., 1999) to set up hydrological inputs.

TOUGHREACT V3.0-OMP provides the following TOUGH2 fluid property or "EOS" (equation-of-state) modules:

- EOS1 for water, or two waters with typical applications to hydrothermal problems
- EOS2 for multiphase mixtures of water and CO_2 also with typical applications to hydrothermal problems
- EOS3 for multiphase mixtures of water and air with typical applications to vadose zone and nuclear waste disposal problems
- EOS4 that has the same capabilities as EOS3 but with vapor pressure lowering effects due to capillary pressure
- EOS7 for multiphase mixtures of water, brine, and air with density and viscosity effects of salinity as an extension of EOS3
- EOS9 for single phase water (Richards' equation) with typical applications to ambient temperature and pressure reactive geochemical transport problems, and
- ECO2N for multiphase mixtures of water, CO_2 and NaCl with typical applications to CO_2 geological storage (sequestration) in deep saline aquifers.

2 Requirements

2.1 Computer Requirements and Code Installation

TOUGHREACT V3.0-OMP is written in FORTRAN 77 with FORTRAN-90 extensions. It has been tested on various computer platforms, including Apple Macintosh Intel-based computers, Microsoft Windows-based PCs, and multiprocessor multi-core Linux clusters. n most machines the code should compile using recent (2013+) Fortran 95 or Fortran 90 compilers. It has been tested using Intel Fortran V15.x on MacOS X and Linux, Intel Fortran V15.x on Windows, and gfortran v4.9 on MacOS X. Executables were all compiled using Intel Fortran V15 or later. TOUGHREACT V3-OMP (like TOUGH2 V2.0) requires 64-bit arithmetic (8 byte word length for floating point numbers) for successful execution. Executables will run on most computers built after about 2008. The TOUGHREACT (V3.0-OMP) source program contains IMPLICIT DOUBLE PRECISION (A-H, O-Z) and IMPLICIT INTEGER*8 (I-N) statements that will automatically generate 64-bit

arithmetic on 32 bit processors. The distribution file folders include documentation (this manual), test problems, executable files and/or source files (depending on the license) generated with compilers described in accompanying README files. Several makefiles for Intel Fortran on a Linux cluster (Intel CPU) are also included.

2.2 OpenMP Usage and Performance

TOUGHREACT V3.0-OMP employs the most recent OpenMP 4.0 framework (http://openmp.org/wp/) for parallelization of chemical reactions and various other cpu-intensive routines. OpenMP is based on the shared memory parallel model. Therefore, all CPUs or cores sharing memory (as on multicore Macs, PCs, and many Linux workstations) are available for the simulation. Basic requirements and usage of OpenMP-based programs are described in this manual.

The speed of codes using parallel processing can increase with the number of cores (or threads), reach a maximum, and then decline as the number of cores increase further. This is expected for all parallel codes, since at some point each core is fast enough to solve more calculations than it takes to spread them out over many cores. For TOUGHREACT V3-OMP, the larger the chemical system, and the greater the number of grid blocks, the more likely the problem will keep increasing in speed (decreasing in time) as the maximum number of cores is reached. The relation depends on several factors, in particular the speed of each core (thread), the memory available, the problem size, the workload distribution, and the time spent for the multiphase flow calculation. Speed increases (in relation to execution on a single core) for some of the example problems are shown in Figure 1 (using a dual quad-core cpu (8 threads) on Mac Pro workstation using MacOS X (10.9)). The theoretical linear increase with the number of cores is shown as the dashed line.
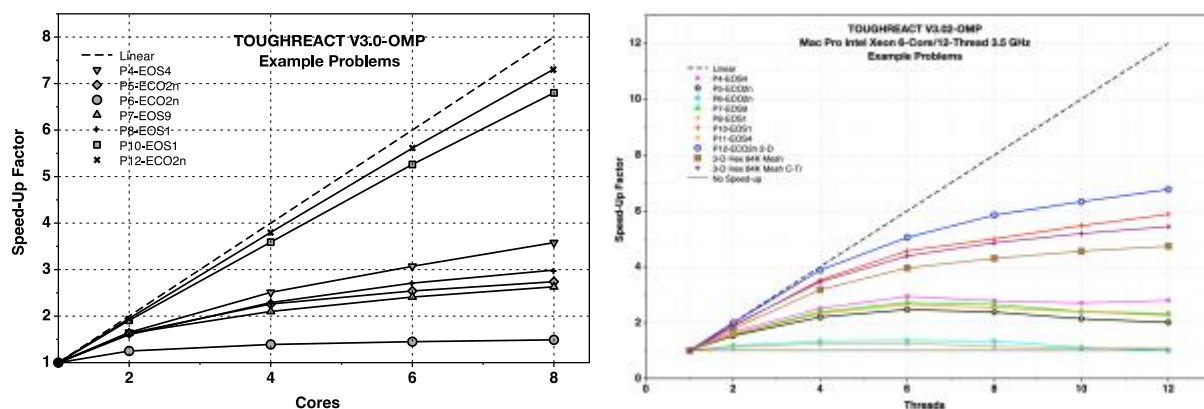
It is advisable to determine how fast the problem runs using the full number of cores on the computer, and also with about half that number for comparison. For those problems running only flow, the number of threads are best set to one, because the primary flow routines are not parallelized and increasing the number of threads will just increase the computational overhead, and actually increase the cpu time.

Setting the number of threads is also useful if you want to run more than one job on your machine and then they won't compete for resources.

Setting the number of threads:

If the number of threads are the computer are unknown, and are not set, the maximum will be used and displayed on the screen. The number of threads can be set on the command line, external to the code inputs, and applies only to the shell where it is invoked. For example, two terminal shells can be opened, one using 2 threads and another using 6 threads, if there are 8 or more threads available. The command to set the number of threads uses the same command to set other environmental variables, as follows:

For example, using a Windows-based PC with the command line:

    set OMP_NUM_THREADS=6

For Linux or Mac OS X using the default bash shell:

    export OMP_NUM_THREADS=6

Under Linux or Mac OS X using tcsh:

    setenv OMP_NUM_THREADS 6

2.3   Memory Requirements

The computer memory required by TOUGHREACT V3.0-OMP depends on the problem size. PARAMETER statements are used in two INCLUDE files: flowpar_v3.inc (for fluid and heat flow dimension parameters)3 and chempar_v3.inc (for reactive chemistry dimension parameters). All major arrays in the problem are automatically adjusted according to these dimension parameters. Different size problems can be modeled by changing the dimensions in the parameter statements, compiling all source files, and linking them to create an executable file. For executable-only distributions, these files are included for reference. At the beginning of a simulation, the program automatically checks the array dimensions related to reactive geochemistry. If the dimensions are insufficient for the specific problem, it typically provides the user with an error message. The memory requirement for these dimensions is typically from 1-2 Gbytes, and for parallel computing, computers should have at least 1 Gbyte per core (thread) available.

2.4   User Knowledge Requirements

The correct implementation, setup, problem formulation, and interpretation of the results of TOUGHREACT requires knowledge of the basic equations of multiphase non-isothermal fluid flow and transport in geologic media and a basic understanding of the numerical solution of the equations that are

used to describe these processes. In addition, the formulation of the geochemical problem requires familiarity with geochemical modeling and an in-depth understanding of the system that is being modeled and of the data used for input to the model. The model boundary conditions, time step length, convergence criteria, and grid properties are crucial elements for a realistic and accurate solution to a problem. The input files for flow parameters are based on TOUGH2 V2.0, with some extensions. However, TOUGH2 V2.0 input files can generally be used little or no modification. A comprehensive reference of TOUGH2 input formats along with illustrative sample problems are provided in the TOUGH2 user's guide, Version 2.0 (Pruess et al., 1999). This information is essential for successful application of TOUGHREACT; it is not duplicated in the TOUGHREACT manual. The file "TOUGHREACT_V3_OMP_QuickRef.pdf" conveniently lists all MOP parameters and their use in TOUGHREACT V3-OMP.

3   Model Description

3.1   Main Scope of the Model

TOUGHREACT V3-OMP (Sonnenthal et al., 2014; Xu et al., 1998; 2006; 2011) is applicable to one-, two-, or three-dimensional geologic domains with physical and chemical heterogeneity and can be applied to a wide range of subsurface conditions. The temperature (T) and pressure (P) limits are controlled by the applicable range of the chemical thermodynamic database, and the limits of the EOS module employed. Thermodynamic databases from external sources are included with the distribution files. Typically, these thermodynamic databases are available for temperatures between 0 and 300°C, at 1 bar below 100°C, and water saturation pressure above 100°C. The temperature and pressure range of thermodynamic data can be extended by changing the thermodynamic database without code modifications. It is the user's responsibility to ensure that the thermodynamic data used with this software is appropriate for the temperature and pressure range of the simulated systems. Water saturation can vary from completely dry to fully water-saturated. The model can deal with ionic strengths from dilute to moderately saline water (up to ionic strengths in the 2–4 molal range, for an NaCl-dominant solution, depending on the system being modeled; see Appendix H for details). The code may run at higher ionic strengths, however, the results may not be qualitatively or quantitatively correct.

TOUGHREACT is applicable to a variety of reactive fluid and geochemical transport problems, including (a) contaminant transport with linear Kd adsorption and radioactive decay (Sample problem 1), (b) natural groundwater chemistry evolution under ambient conditions (Sample 2), (c) assessment of nuclear waste disposal sites (Samples 3, 4, and 11), (d) CO_2 geological storage in deep formations (Samples 5 and 6), (e) mineral deposition such as supergene copper enrichment (Sample 7), and (f) mineral alteration and silica scaling in hydrothermal systems under natural and production conditions (Sample 8), and biogeochemical transport and environmental remediation (Samples 9 and 10).

3.2   Major Processes

The major processes for fluid and heat flow are: (1) fluid flow in both liquid and gas phases occurs under pressure, viscous, and gravity forces; (2) interactions between flowing phases are represented by characteristic curves (relative permeability and capillary pressure); (3) heat flow by conduction and convection, and (4) diffusion of water vapor and air. Thermophysical and geochemical properties are calculated as a function of temperature, such as fluid (gas and liquid) density and viscosity, and thermodynamic and kinetic data for mineral-water-gas reactions. Transport of aqueous and gaseous species by advection and molecular diffusion are considered in both liquid and gas phases. Depending on the computer memory and CPU performance, any number of chemical species in the liquid, gas and solid phases can be accommodated. Aqueous and surface complexation, acid-base, redox, gas dissolution/exsolution, and multi-site cation exchange are considered under the local equilibrium assumption. Mineral dissolution and precipitation proceed under either equilibrium or kinetic constraints (Xu et al., 1999b). Intra-aqueous kinetics and biodegradation (Xu, 2008; Xu et al., 2009b; Spycher et al., 2009) and surface complexation using non-electrostatic, constant capacity and double layer electrostatic models (Zheng et al., 2009), were incorporated into Version 2 of TOUGHREACT. Linear adsorption and simple decay can be also included.

3.3   Governing Equations

The primary governing equations for multiphase fluid and heat flow, and chemical transport have the same structure, derived from the principle of mass (or energy) conservation. These equations are presented in Appendix A. Expressions for non-isothermal multiphase flow are given in Pruess (1987) and Pruess et al. (1999). The transport equations are written in terms of total dissolved concentrations of chemical components, which are concentrations of the basis species plus their associated aqueous secondary species (Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Walter et al., 1994; Lichtner, 1996; and Xu and Pruess, 2001b). If kinetically-controlled reactions occur between aqueous species, then additional ordinary differential equations need to be solved to link the total concentrations of the primary species with the evolving concentrations of the secondary species (Steefel and MacQuarrie, 1996). Kinetically-controlled reactions between aqueous species are considered in the present version. Slow aqueous phase reactions are common in the case of redox reactions. Advection and diffusion processes are considered for both the aqueous and gaseous species. Aqueous species diffusion coefficients are assumed to be the same. Gaseous species, having a neutral valence, can have differing diffusion coefficients calculated as a function of T, P, molecular weight, and molecular diameter. The local chemical interactions in the transport equations are represented by reaction source/sink terms.

The primary governing equations must be complemented with constitutive local relationships that express all parameters as functions of fundamental thermophysical and chemical variables. The equations for chemical reactions are presented in Appendix B. Mass conservation in the closed chemical system is written

in terms of basis (component) species. The species distribution must be governed by the total concentrations of the components. The oxygen is used for formulating redox reactions by attributing the oxidizing potential to the dissolved oxygen (Nordstrom and Muñoz, 1986; Wolery, 1992). In contrast to the free electron in the hypothetical electron approach (Yeh and Tripathi, 1991), oxygen can be present and can be transported in natural subsurface flow systems. The formulation for cation exchange is similar to that of Appelo and Postma (1993). For intra-aqueous kinetic reactions, sorption kinetic reactions, and biodegradation, a general-rate law that can deal with multiple mechanisms and multiple products, Monod, and inhibition terms (Xu et al., 2008), is used (Appendix B). For kinetically-controlled mineral dissolution and precipitation, a general form of the rate law (Lasaga, 1984; Steefel and Lasaga, 1994; Palandri and Kharaka, 2004) is used (Appendix B). Thermodynamic and kinetic data are functions of temperature.

Temporal changes in porosity, permeability, and unsaturated hydrologic properties owing to mineral dissolution and precipitation can modify fluid flow. This feedback between transport and chemistry can be important (e.g., Raffensperger, 1996), and can be treated by TOUGHREACT. Changes in porosity during the simulation are calculated from changes in mineral volume fractions. The porosity-permeability correlation in geologic media can be complex, depending on several factors, such as pore size distribution, pore shapes, connectivity (Verma and Pruess, 1988), and crystal morphology. Several porosity-permeability and fracture aperture-permeability relationships are included in the model (Appendix F). The code can also be set to monitor changes in porosity and permeability during the simulation without considering their effects on fluid flow. In unsaturated systems, capillary pressure can be modified via permeability and porosity changes using Leverett scaling (based on Slider, 1976).

3.4   Simplifying Approximations

Hydrodynamic dispersion can be an important solute transport phenomenon that arises from subgrid-scale differences in flow velocity in different pathways (e.g., pores, capillaries, or fractures). This process is not currently explicitly implemented in TOUGHREACT V3-OMP for various reasons, one of which being that typical representations of this process (such as Fickian dispersion models) have fundamental flaws and limitations, as demonstrated in numerous studies in the hydrogeology literature over the last twenty years. The numerical approximations used in TOUGHREACT V3-OMP can introduce some spatial and temporal numerical dispersion, and thus adding hydrodynamic dispersion may result in excessive dispersion. In addition, molecular diffusion can be modeled explicitly in TOUGHREACT V3-OMP, which often is lumped into a single "hydrodynamic dispersion parameter" as determined from field transport studies. As necessary, hydrodynamic dispersion can be modeled through appropriate spatial resolution on multiple scales, using multiple continua (or multi-region) models (Pruess and Narasimhan, 1985; Gwo et al., 1996; Sonnenthal et al., 2005) or explicit incorporation of fine-scale permeability heterogeneity (Mukhopadhyay et al., 2009) to describe interactions between fluid regions with different velocities.

Changes in thermophysical properties of fluid phases (such as viscosity, surface tension, and density) as a function of the fluid chemical composition are not considered in TOUGHREACT V3-OMP. Pressure effects on chemical equilibrium constants are typically neglected; however, molar volume data for specific reactions can be introduced in the thermodynamic database for pressure corrections to be included (Section 6.4).

4 Solution Method

Figure 4—1   Flow chart of the TOUGHREACT program

This figure shows the flow chart for solving coupled non-isothermal multiphase fluid flow, solute transport, and reactive geochemistry in TOUGHREACT. Boxes shaded in yellow are the primary parts of the code that run in parallel using OpenMP V4.0. Some other routines are partially parallelized.

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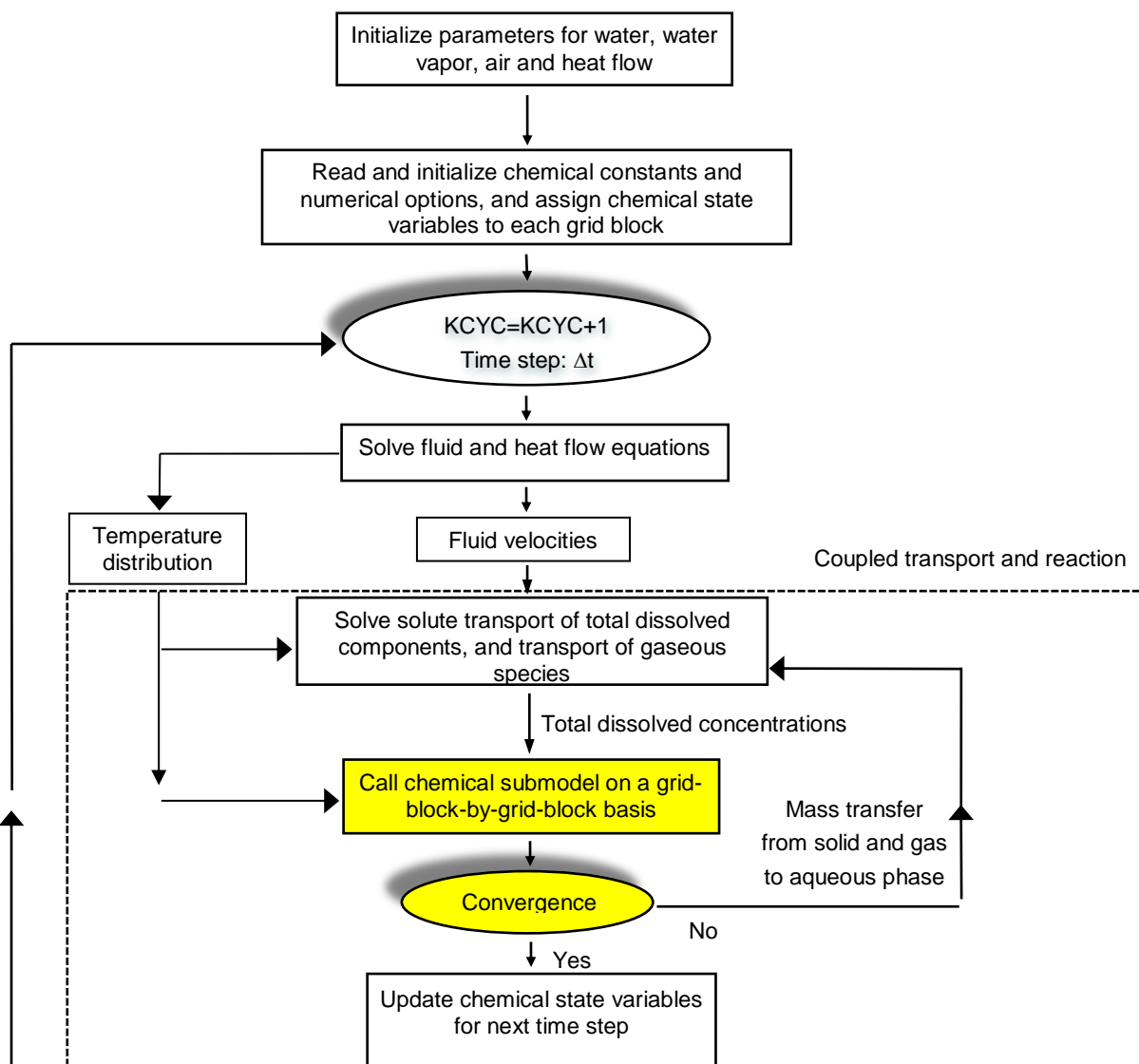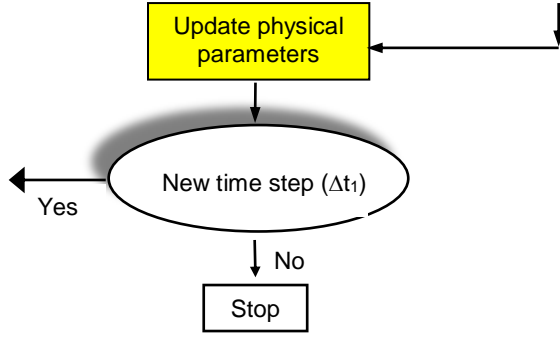
The numerical solution of multi-phase fluid and heat flow proceeds as in TOUGH2. Space discretization is employed by means of integral finite differences (IFD; Narasimhan and Witherspoon, 1976). Because chemical transport equations (derived from mass conservation) have the same structure as fluid and heat flow equations, the transport equations can be solved by the same numerical method. The discretization approach used in the IFD method and the definition of the geometric parameters are illustrated in Figure 4-2. The basic mass- (for water, air, and chemical components) and energy- (for heat) balance equations are written in integral form for an arbitrary domain V_n

$$V_n \frac{\Delta M_n}{\Delta t} = \sum_m A_{nm} F_{nm} + V_n q_n$$

(4.1)

where subscript n labels a grid block, subscript m labels grid blocks connected to grid block n, Δt is time step size, and M_n is the average mass or energy density in grid block n. Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}, F_{nm} is the average flux (of mass or energy) over the surface segment A_{nm} between volume elements n and m, and q_n is the average source/sink rate in grid block n per unit volume. Time is discretized fully implicitly as a first-order finite difference to achieve unconditional stability. More detail on the numerical discretization is given in Pruess et al. (1999). The IFD method gives a flexible discretization for geologic media that allows the use of irregular unstructured grids, which is well suited for simulation of flow, transport, and fluid-rock interaction in multi-region heterogeneous and fractured rock systems. For systems with regular grids, IFD is equivalent to conventional finite differences.

Figure 4—2   Space discretization and geometric data for the integral finite difference method
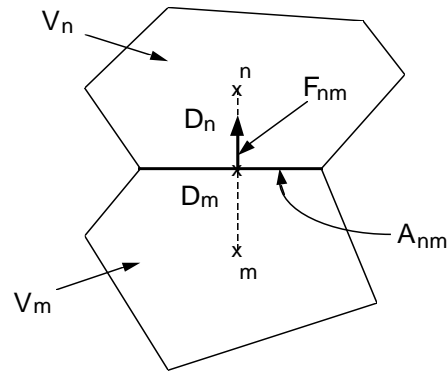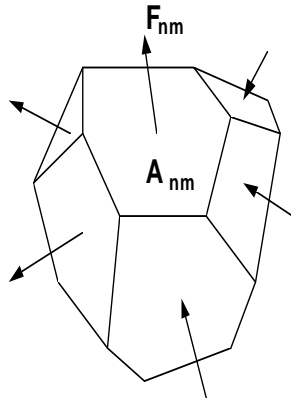
The time discretization of fluid and heat flow equations results in a set of coupled non-linear algebraic equations for the unknown thermodynamic state variables in all grid blocks. These equations are solved by Newton-Raphson iteration as implemented in the original TOUGH2 simulator (Pruess, 1991). The set of coupled linear equations arising at each iteration step is solved iteratively by means of preconditioned conjugate gradient methods (Moridis and Pruess, 1998).

TOUGHREACT uses a sequential iteration approach (SIA) similar to Yeh and Tripathi (1991), Engesgaard and Kipp (1992), Simunek and Suares (1994), Walter et al. (1994), Steefel and Lasaga (1994), Sonnenthal and Ortoleva (1994), and Sonnenthal and McBirney (1998). After solution of the flow equations, the fluid velocities and phase saturations are used for chemical transport simulation. The chemical transport is solved on a component-by-component basis (details on the solution method are given in Appendix C). The resulting concentrations obtained from solving transport equations are substituted into the chemical reaction model. The system of mixed equilibrium-kinetic chemical reaction equations is solved on a grid block by grid block basis by Newton-Raphson iteration (details are given in Appendix D). Optionally, the reactive surface areas, chemical transport and reactions are solved iteratively until convergence.

After chemical convergence, the porosity, permeability, and for multiphase systems, the capillary pressure can be updated owing to mineral-water reaction volume changes. Moles of water and/or CO_2 consumed or liberated by chemical reactions are also stored for possible effects on source terms for multiphase fluid flow in the following time step.

As an alternative to the sequential iterative approach, a sequential non-iterative approach (SNIA) may be used, in which the sequence of transport and reaction equations is solved only once (Walter et al., 1994; Steefel and MacQuarrie, 1996; and Xu et al., 1999a). Xu et al. (1999a) analyzed the accuracy of SIA and SNIA using several test cases. They concluded that the accuracy of SNIA depends mainly on the Courant number, which is defined as $C = v\Delta t/\Delta x$, where v is fluid velocity and Δx is grid spacing. For small Courant numbers, satisfying the stability condition $C \leq 1$, the differences between SNIA and SIA are generally small.

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The accuracy of SNIA also depends on the type of chemical process. Therefore, the applicability of the decoupling of chemical reactions from transport will depend on time and space discretization parameters, the nature of the chemical reactions and the desired accuracy. When SNIA is used, the Courant number condition $C \leq 1$ can be automatically enforced during the simulation.

An automatic time stepping scheme is implemented in TOUGHREACT, which includes an option to recognize "quasi-stationary states" (QSS; Lichtner, 1988) and perform a "large" time step towards the end of a QSS.

For analyzing water flow through partially saturated porous media, the gas phase may often be considered a passive bystander and not be represented explicitly (Richards, 1931). This means that for the purpose of solving for water flow, the entire gas phase is at the same pressure (usually the atmospheric pressure). TOUGHREACT allows a choice of considering saturated-unsaturated liquid phase flow in which case only molecular diffusion is considered for gaseous species transport. Alternatively, the full non-isothermal multiphase flow equations (liquid, gas, and heat) may be solved. To test the passive gas phase approach under ambient conditions, Xu et al. (2000) performed numerical simulation experiments on pyrite oxidation in a variably saturated porous medium. They found that under ambient conditions the effects of partial pressure reduction due to oxygen consumption on the fluid flow is not significant, and oxygen diffusion is the dominant gas phase transport process. However, when fluid flow and chemical reactions are strongly coupled, as e.g. in boiling hydrothermal reservoirs, gas phase advection could be essential (White, 1995).

5   General Description of Input and Output Files

5.1   Input Files

Three user-specified input files are required. The input file names have been fixed in the program (i.e., names cannot be specified by the user). Descriptions of these input files are given below. Details on input formats and contents are given in Chapter 6.

flow.inp – Flow input. The arbitrary input file name for TOUGH2 was changed to the fixed filename "flow.inp" to simplify execution. This file mainly includes rock properties, time-stepping information, geometric grid information, initial and boundary conditions, and data related to a multiphase fluid and heat flow simulation. The flow input is in most cases compatible with the original TOUGH2 V2 (see the manual; Pruess et al., 1999), with an additional data block REACT (see Section 6.1), and a several other extensions. This is a "fixed" format file.

solute.inp – Transport, zone assignment, output, convergence, and other run parameters. This file contains various flags and input parameters for calculations of reactive transport, such as diffusion coefficients, tolerance limits for convergence of transport and chemical iterations, flags for printout of minerals and aqueous species, and the assignment of model zones with different chemical properties (the properties of each zone, however, are given in file chemical.inp described below). Some minor additions were made for TOUGHREACT V3-OMP, and therefore solute.inp used for earlier code versions must be updated. This is a "free" format file.

chemical.inp – Chemical parameters and properties. This file is used to define the chemical system (i.e. the type and number of aqueous component species, minerals, gases, and sorbed species considered in the simulation). It also includes the initial compositions of water, minerals, and gases in zones that are assigned to grid blocks in file solute.inp, and kinetic data for intra-aqueous reactions and minerals (rate constants, surface areas, etc.). Some minor additions were made for TOUGHREACT V3-OMP, and therefore chemical.inp used for earlier code versions must be updated. This is "free" format file.

In addition to the above-mentioned three input files, the program requires a thermodynamic database file with a file name specified in the solute.inp file. This file contains reaction stoichiometries, dissociation constants (log(K)), and regression coefficients of log(K) as a function of temperature and pressure (see Section 6.4 for details). Version 3.0 optionally includes mineral heat capacity coefficients, thermal conductivity coefficients, and thermal expansion parameters. The thermodynamic database is also a "free" format file.

5.2   Output Files

Two types of output files are generated from TOUGHREACT V3-OMP: (1) fixed file names, and (2) user-specified file names.

5.2.1   Fixed name output files

flow.out – Flow output. This file is very close to the TOUGH2 V2 output file, including data on temperature, pressure, liquid saturation, mass flux, and phase velocities for all grid blocks of the model.

solute.out – Echo of input file solute.inp. This file lists data that was read from input file solute.inp, including all transport parameters, chemical zone configuration, and other run-specific parameters.

chemical.out – Echo of input file chemical.inp. This file lists data that was read from input files chemical.inp and the thermodynamic database, including initial water, rock, and gas compositions, equilibrium constants and stoichiometries of chemical reactions, kinetic data, and linear adsorption Kd values and decay constants for certain species.

runlog.out – Log of the simulation progress. This file is updated throughout the simulation. It lists some run input parameters and all run-related messages, including error messages (Chapter 7).

chdump.out – chemical speciation data. This file contains results of geochemical speciation calculations for each initial water composition input into the model, including a printout of chemical mass balances (total mass balance and aqueous species mass balance). It also lists these data for grid blocks where chemical convergence fails (not reaching the specified convergence criteria). For debugging purposes, or for small number of grids, the flag ICHDUMP in the solute.inp input file allows geochemical speciation results to be output in the *chdump.out* file for every grid block, or certain specific grid blocks, at time step intervals. As a precaution to avoid filling up disk space, results of speciation calculations are output only for the first thousand grid blocks and/or time steps, after which output in this file is suspended.

savechem – save of geochemical data for restart. This file can be used to restart a TOUGHREACT run from the end of a previous run. Geochemical conditions obtained in one run are written to disk file *savechem*, and can be used as initial conditions in a subsequent run. The restart run for reactive geochemical transport simulation must be used together with a restart of the flow simulation (see p. 61 of the TOUGH2 V2 manual; Pruess et al., 1999). For a restart run, the name of file *savechem* must be changed to *inchem*, and the name of file *SAVE* to *INCON* (same as in the original TOUGH2). In Version 3.0, the initial permeabilities and porosities from the first simulation in the run sequence is saved so that permeability changes after multiple restarts are correctly calculated. Therefore, *savechem* files created with previous TOUGHREACT versions cannot be used to restart a TOUGHREACT V3-OMP simulation.

In addition, TOUGHREACT V3-OMP creates the following optional fixed-name output files:

min_SI.out – mineral saturation indices
rct_sfarea.out – mineral reactive surface areas
rctn_rate.out – mineral reaction rates
mbalance.out – chemical mass balance information
thermalparam.out - mineral and rock thermal conductivities and heat capacities (new in V3.0)
heatreaction.out - mineral and bulk system heats of reaction (new in V3.0)
wellbore.out – Reynolds #, friction, permeabilities at wellbore elements/connections (new in V3.0)

 Printing of these files is controlled by parameter MOPR(8) in the *flow.inp* file, described in Section 6.1.

5.2.2   User-specified output files

The names of these files must be specified in the input file *solute.inp*, and cannot be left blank. The output files are described below:

Iteration data (e.g., *iter.out*): Number of flow, transport, and chemical iterations used to reach convergence at some time steps.

Aqueous species data (e.g., *aqconc.tec*): This file contains times, grid block coordinates (m), gas and liquid saturations, temperature (°C), pH, and aqueous species concentrations at all grid blocks for times specified in the flow.inp file. The number and types of species output are specified by flags in the input file solute.inp. This file has a TECPLOT-compatible format.

Solid phase data (e.g., *minerals.tec*): This file contains time, grid point coordinates (m), temperature (°C), mineral abundance, and exchanged species concentrations at all grid blocks for time printout intervals specified in the flow.inp file. This file has a TECPLOT-compatible format.

Gas phase data (e.g., *gases.tec*): Time, grid point coordinates (m), temperature (°C), and gas partial pressures for all grid blocks at times specified in the flow.inp file. This file has a TECPLOT-compatible format.

Plot data at specified grid blocks (time evolution) (e.g., *time.out*): This file contains the grid block identifier, time, gas and liquid saturations, temperature, pH, aqueous species concentrations, mineral abundances, gas pressures, and exchanged species concentrations for specific grid blocks and time intervals, as specified in the input file solute.inp.

6   Input File Formats and Contents

6.1   Flow Input (flow.inp)

Input formats for multiphase flow are similar to TOUGH2 Version 2.0 (Pruess et al. 1999), with several new features and the addition of keyword block 'REACT' for invoking a reactive transport simulation. The REACT block has one record that specifies option parameters related to reactive transport. Without this data block, the program runs a multiphase flow simulation only. In TOUGHREACT V3.0-OMP, additional options are present in keyword blocks 'ROCKS', 'PARAM', 'INCON', 'CONNE', and 'GENER' from TOUGH2 V2.0. Inputs for these options are discussed below. Also note that the TOUGH2 capability of defining an "inactive" grid block with a zero or negative volume in the input block 'ELEME' (used for a constant boundary condition), is not operational in TOUGHREACT. Instead, constant chemical boundary conditions are set in TOUGHREACT by input of a very large volume ($\geq 10^{20}$ m^3) for boundary grid blocks. Chemical concentrations in these grid blocks will not undergo speciation or mineral-gas-water-reactions, and pressure and temperature will also remain constant (for volumes $\geq 10^{50}$ m^3). In TOUGH2 V2.0, setting the volume to greater than 10^{50} will also remove the boundary grid blocks from mass balance calculations.

TOUGHREACT V3-OMP also incorporates some options of other TOUGH2 versions that were developed specifically for unsaturated flow and boiling in fractured rock. The additions to the flow input file are given below.

REACT Parameter choices for reactive transport simulation

Variable: MOPR(20)

Format: 20I1

MOPR(1)   = 0 perform reactive transport

= 1 no reactive transport, but input files with chemical data are read

= 2 no reactive transport, no chemical data files are read

= 3 solves flow and transport without chemical reaction

= 4 solves transport and chemical reactions using constant velocity field (flow calculated at first time step only)

= 5 solves transport (no chemical reactions) using constant velocity field (flow calculated at first time step only)

MOPR(2)   > 0 writes the transport coefficient matrix, Darcy velocities, porosities, and other transport data in the runlog.out file during calculations of aqueous species and gas transport. Primarily used for debugging (very large output!).

MOPR(3)   > 0   writes source terms, old and new aqueous concentrations, and various other parameters in the *runlog.out* file during transport calculations. Also outputs the permeability, porosity, and capillary pressure correction factor at each grid block in the *runlog.out* file. Primarily used for debugging (very large output!).

MOPR(4)   ≠ 1 Force at least one fluid flow step to be calculated (MOPR(4) =2 is normally suggested) .

= 1 does not force at least one fluid flow step to be calculated. This option can be useful to compute chemical reactions in single-grid block problems. When the chemical quasi-stationary states (QSS) option is considered, MOPR(4) must be set equal to one.

MOPR(5)   = 0 Results in printout of time step iteration information in flow.out, as in TOUGH2 V2. The use of this option is normally suggested unless the file *flow.out* becomes too big. In the latter case, use MOPR(5)=1 option.

= 1 No printout at every time step in flow.out.

MOPR(6)   = 0 No Leverett scaling of capillary pressure

= 1 Leverett scaling of capillary pressure assuming capillary flow (Eq. F.9a in Appendix F) for heterogeneous porosity and permeability fields and/or from porosity-permeability changes owing to mineral dissolution and precipitation.

= 2 Leverett scaling of capillary pressure assuming channel (e.g., fracture) flow (Eq. F.9b in Appendix F).

= 3 Leverett scaling of capillary pressure assuming mixed capillary and channel (e.g., fracture) flow with the function linearly weighted by the porosity (porosity of 1.0 yields pure channel flow scaling, tending to pure capillary flow scaling as the limit of zero porosity is approached; see Appendix F).

MOPR(7)   ≥ 0 Allow the specification of the number of digits past the decimal in tecplot-format output files (up to 8 digits). For accurate ratios of components or calculation of isotopic ratios it is usually necessary to write out at least 6 digits. Zero or blank gives the default of 4 digits.

MOPR(8)   = 0 No printout of extra output files.

≥ 1 Outputs mineral saturation indices, for each grid block, in file *min_SI.dat*. This information is output at the same intervals as specified in *flow.inp* for the flow (and chemistry) information.

≥ 2 Creates an additional output file (at same time intervals as above) with mineral reaction rates (mol/kg H_2O/s) at all grid blocks. The file name is fixed as *rctn_rate.out*.

≥ 3 Creates an additional output file (at same time intervals as above) with mineral reactive surface areas (m^2/kg H_2O) and other parameters (e.g., active fracture parameter) for liquid saturation-dependence that are used in the rate equation after all conversions. The file name is fixed as *rct_sfarea.out*.

≥ 4 Outputs mass balance information in file *mbalance.out*.

≥ 5 Outputs thermal conductivities and heat capacities (Cp) of minerals, and calculated rock Cp coefficients from mineral values in file *thermalparam.out*.

≥ 6 Outputs system and mineral heats of reaction in file *heatreaction.out*.

MOPR(9): = 1 Use heat capacities of minerals based on data in thermodynamic database to calculate rock heat capacity. See Appendix XX for details.

= 2 Use thermal conductivities of minerals based on data in thermodynamic database to calculate rock value. See Appendix XX for details.

= 3 Temperature-dependent mineral heat capacities and thermal conductivities used to calculate rock values

MOPR(10) ≥ 1 The time step length will NOT be shortened if chemical convergence is slow (i.e., no time-step control by chemistry)

MOPR(11) = 1 Enables approximating sedimentation/compaction processes by forward explicit advection of solids and aqueous species. If enabled, a sedimentation velocity (constant in time but optionally variable with depth) must be entered in record 11 and 12 of file *solute.inp* (Section 6.2). This option works only for a vertical 1D column with grid blocks and connections ordered sequentially from top to bottom (this option is only beta-tested !).

MOPR(12) = 1 Heat of reaction source terms calculated from log (K) values in thermodynamic database are included in heat flow calculations (uses sequential noniterative approach). See Appendix XX for details.

MOPR(13) = 1 Temperature-dependent mineral and rock densities are calculated based on thermal expansion coefficients read in from thermodynamic database (placeholder- not fully implemented yet).

MOPR(14) ≥ 1 Exponent to apply to writing out SAVE and savechem files. NTSAVE (dimensioned to 100 in flowpar_v3.inc) is modified according to NTSAVE*(10**MOPR(14)), such that the default of MOPR(14)=0, gives the increment of printout as every 100 time steps.

MOPR(15) = 1 Permeability will be modified according to the domain "SEED" specified in file *flow.inp* (see the TOUGH2 V2 manual).

MOPR(16) = 1 Enables reading a heterogeneous field of mineral volume fractions. n ascii input file with name *min_volf.inp* must be provided in addition to the other input files. This file must contain a header in record 1, immediately followed (starting in record 2) with one record per mesh gridblock (for all gridblocks in the mesh) in the same gridblock order as specified in file *flow.inp* (or *MESH*). Each of these records must include, separated by blanks: gridblock ID (format A5); dry initial volume fraction of each mineral (free format), in the same mineral order as specified in the input file *chemical.inp*. Only works in conjunction with the properties of the first rock in chemical.inp.

MOPR()-MOPR(20):   Not currently used. Leave blank.

PARAM

PARAM.1

The meaning of variable MCYC (maximum number of time steps to be calculated) in Record was extended slightly from the original TOUGH2. In TOUGHREACT, if MCYC = 9999, the number of time steps is not controlled by MCYC, and therefore the maximum simulation time is only controlled by TIMAX in Record PARAM.2. IF MCYC $\leq$ 9998, it is the same as in TOUGH2 V2.

MOP Value Changes

MOP(14) = 0 Fixed rock thermal conductivities and heat capacities (uses values in ROCKS as in TOUGH2 V2.0)

= 1 Temperature-dependent rock grain heat capacities will be used if entered in ROCKS (4 coefficients (E14.6) line 4)

= 2 Temperature-dependent bulk rock thermal conductivity will be used if entered in ROCKS (3 coefficients (E10.4) line 3).

= 3 Both temperature-dependent rock thermal conductivity and heat capacity calculated as described above

MOP(17) $\geq$ 1 Invoke single-phase wellbore simulator for turbulence and momentum effects on pressure through revised permeability scheme based in part on Battistelli et al. (2011), with two options for numerical convergence. When invoked, the initial wellbore permeability is assumed to be in permeability direction '3'. This wellbore permeability is used to calculate the wellbore diameter assuming Poiseulle flow. Only grid block connections designated as 'ISO=5' in CONNE will be subject to wellbore flow calculations. Details are given in Appendix XX.

= 1 Wellbore permeability at current iteration is calculated from the average value calculated from the current turbulence/friction calculation and the value from previous iteration. This option is normally recommended.

= 2 Wellbore permeability at current iteration is calculated from geometric mean of the value calculated from the current turbulence/friction calculation and the value from previous iteration.

PARAM.2

Variable ELST in record was modified so that if the keyword "wdata" is used the program will look for a line after PARAM.2 giving the number of grid blocks to write out specific flow data. Following the integer variable, the 5 character identifiers for the grid blocks must be listed sequentially in column format. The name of the output file is fixed as GASOBS.DAT. The records PARAM.3 and PARAM.4 should follow immediately after the last grid block name. An example is shown below.

```
PARAM            12345678901234578901234
   29999    99990000000001200000471005000   2.14e-5      2.334
 0.00000  0.157785e8     1.e+006.0480e+05wdata       -9.806650
3
wp001
dr357
d2357
 1.0000e-4
 0.0000000000000D+00  0.0000000000000D+00  0.0000000000000D+00
```

Also note a minor format difference for Record PARAM.4 for default initial conditions (inconsequential change from E20.14 to E20.13):

Format (4E20.13)

DEP(I), I = 1, NKIN+1

ROCKS The following hydrological property options were added to those in TOUGH2 V2 (Pruess et al., 1999) within the ROCKS input records.

ROCKS 1.1

Format (9E10.4)   (TORTX was modified and PTORT and PHICRIT were added)

COM, EXPAN, CDRY, **TORTX**, GK, XKD3, XKD4, **PTORT**, **PHICRIT**

TORTX < 0 Generalized power law (Burnol and Claret, 2012; Lagneau, 2002) with saturation-dependence added. For direct porosity or saturation-porosity dependence, set TORTX = -1.0. If TORTX < 0, then PTORT and PHICRIT must be set. For TORTX = 0.0, the option reverts to the Millington-Quirk formulation as in TOUGH2 V2. If TORTX > 0.0 then tortuosity is a fixed value, as in TOUGH2 V2.

PTORT   Exponent for generalized power law. Required for TORTX < 0, and is an added parameter in the ROCKS 1.1 line (entries 71-80).

PHICRIT   Critical porosity for generalized power law. Required for TORTX < 0, and is an added parameter in the ROCKS 1.1 line (entries 81-90).

ROCKS 1.2 (If "NAD" greater than or equal to 3)

Format (I5,5X,3E10.4)

ITP, TCONDPAR(1), TCONDPAR(2), TCONDPAR(3)

ROCKS 1.3 (If "NAD" greater than or equal to 3)

Format (I5,5X,4E14.6)

IHCPLAW, CPRKCF(1), CPRKCF(2), CPRKCF(3), CPRKCF(4)

ROCKS 1.2 or ROCKS 1.4

RP(5) > 0.0 This option, with IRP = 7 and RP(4) = 0.0, enables the modified Brooks-Corey for gas relative permeability, as implemented by Wu et al. (1999). Note that RP(4) must be smaller than or equal to zero if this option (RP(5) > 0.0 is used.

ROCKS 1.3 or ROCKS 1.5

ICP = 10 Capillary pressure linearization at small liquid saturations, as implemented in Wu and Mishra (1998). With this option, the input parameters CP(I) are the same as for the Van Genuchten function option (ICP = 7), except that CP(4) is set to parameter *epsilon* instead of P_{max}. In this case, the capillary pressure is linearly extrapolated from $S_l = S_r$ + *epsilon* (with S_l and S_r being the current and residual liquid saturations, respectively) down towards S_l = 0. The slope of the linear extrapolation corresponds to the slope of the capillary-pressure/liquid-saturation function at $S_l = S_r$ + *epsilon*.

CP(6) > 0.0 This option, with either ICP = 7 or ICP = 10, and together with flag ISOT = –10 in the CONNE first input record, enables the active fracture model (Liu et al., 1998) as implemented by Wu et al. (1999). In this option, CP(6) is used to input the active fracture parameter γ.

INCON Three variables for three components of permeability were added to Record INCON.1 after porosity PORX (..., PORX, *PER1, PER2, PER3* with format ..., E15.9, *3E15.9*). Like porosity, if zero or blank, three values of permeability will be taken as specified in block 'ROCKS' if option START is used. If the values of porosity and/or permeability are different in INCON and ROCKS then the ratios will be used for calculation of modified capillary pressures if the Leverett scaling option is selected (MOPR(6)=1). If zero or blank, temperature will be taken as default value specified in block 'ROCKS'. The SAVE file will also include the updated porosity and permeability values resulting from mineral precipitation or dissolution.

A minor format difference is present in Record INCON.2 (inconsequential change from E20.14 to E20.13):

Format (4E20.13)

X1, X2, X3, X4

For use of the EOS9 flow module, in Record INCON.2 the second primary variable X2 is used for specifying grid block dependent temperature (in °C). This allows for variable gas species diffusion coefficients and chemical calculations to be performed assuming a fixed temperature field.

As explained in the TOUGH2 manual for restarts (Pruess et al., 1999, p. 61–62, 169), when record INCON.3 starts with the string '+++', the code will look for time stepping information in one additional record. This record is generated by the code and is output in file SAVE. This additional record has been modified slightly to the following format:

Format (2I6, I3, 2E15.8)

KCYCX, INTERCX, NMX, TSTX, TIMINX

where KCYCX is the total (cumulative) number of time steps at the current time, INTERCX is the total (cumulative) number of iterations at the current time, NMX is the total number of rock types in

the present simulation, TSTX is the prior starting simulated time, and TIMINX is the current simulated time (i.e. when the SAVE file was generated).

MESH Reading and writing the indexing for MESH files for 100,000 to 999,999 grid blocks extends the functionality of TOUGHREACT to problem sizes larger than 99,999 grid blocks. No flag is required, and TOUGHREACT will read MESH files created from TOUGH2 V2.0 and prior TOUGHREACT versions and create the revised indexing on output.

CONNE Variable 'ISO' has an optional value of '5' which identifies the grid blocks to be considered as part of a single-phase wellbore simulation if MOP(17) ≥ 1.

GENER An option was added for time-dependent thermal conductivity. For this option, one more parameter, KTAB, was added at the end of record GENER.1:

Format (A3, I2, A3, I2, 4I5, 5X, A4, A1, 3E10.4, I2)

EL, NE, SL, NS, NSEQ, NADD, NADS, LTAB, TYPE, ITAB, GX, EX, HX, KTAB

KTAB is the number of points (number of time values and same number of factors) to read in following records for time-dependent thermal conductivities (variables before KTAB are unchanged from Pruess et al., 1999, p. 174).

If KTAB > 0, the following sets of time values and factors are read:

Record GENER.1.4 (format unchanged from GENER.1.1):

Format (4E14.7)

TIMKTH (1:KTAB)

TIMEKTH (1:KTAB) are the time values ("generation times") at which thermal conductivity values change

Record GENER.1.5:

Format (4E14.7)

FACKTH (1:KTAB)

FACKTH (1:KTAB) are the values of the time-dependent factors corresponding to the list of time values given in GENER.1.4. At each time values specified in record GENER.1.4, the thermal conductivity (determined from wet and dry conductivity values input in records ROCKS.1 and ROCKS.2) is multiplied by these factors.

Reading and writing the indexing for GENER files for 100,000 to 999,999 grid blocks was added for consistency with the MESH file. No flag is required, and TOUGHREACT will read GENER files created from TOUGH2 V2 and prior TOUGHREACT versions.

6.2   Transport Input (solute.inp)

Except for non-numeric variables (title, grid block names, and names of species and minerals), data from this file are read in free format. The first input record to be read in this file is the title. It is followed by

14 main data records. "Skip" records (see below) can be included anywhere in the file, as long as not within a sequence of array inputs of the same variable (e.g., list of species, or list of gridblocks). Some records can be omitted in certain conditions. Some variables in data records are not required under certain conditions. In such cases, one should input them as zero values. Each record is described below, including the description of each input variable and its corresponding FORTRAN format for appropriate reading.

"Skip" records:

> One or more heading (comment) line can precede each record described below (see inputs of the sample problems, such as in Figure 8.1-3). The comment line is indicated by beginning with "#" followed by one blank (without quotes), or any blank record. These records will be skipped on input, and can be inserted anywhere in the file. These "skip" records can be also used for data source references, or other purpose.

Record_1. Title

> Variable: TITLE
>
> Format: A82
>
> TITLE: title and comments.

Record_2. Options for reactive geochemical transport (1)

> Variable: ISPIA ITERSFA ISOLVC NGAMM NGAS1 ICHDUMP KCPL ICO2H2O iTDS_REACT
>
> Format: 9I (integer free format)
>
> ISPIA : flag for iteration scheme between transport and reaction. ISPIA = 2 is much faster and
> more commonly used, but ISPIA = 0 gives a more accurate result at each time step
> > 0   Sequential iteration between transport and chemistry
> > 2   No sequential iteration (fully explicit reaction source terms)
>
> ITERSFA : Reactive surface areas are calculated either outside or inside the chemical reaction
> Newton-Raphson iterations.
> > 0   Reactive surface areas calculated outside Newton-Raphson iterations.
> > 1   Reactive surface areas calculated inside Newton-Raphson iterations.
>
> ISOLVC : flag for the linear equation solver for transport. The solvers are the same as in TOUGH2
> V2 (see p. 73 of the manual, Pruess et al., 1999), except for the removal of MA28. ISOLVC = 3
> or 5 are often used, and in some cases DLUSTB (5) converges where other solvers fail
> > 2 - DSLUBC, a bi-conjugate gradient solver
> > 3 - DSLUCS, a Lanczos-type bi-conjugate gradient solver
> > 4 - DSLUGM, a general minimum residual solver
> > 5 - DLUSTB, a stabilized bi-conjugate gradient solver
>
> NGAMM : flag for sub-iteration between calculation of activity coefficients and secondary species
> concentrations at the beginning of each chemical Newton-Raphson iteration. NGAMM is the
> number of subiterations. For most problems this should be set to zero (which internally
> implements a default value of 2). If convergence of the Newton-Raphson iterations for the

chemical system fails, increase NGAMM up to a maximum of about 4. Note that increasing this parameter significantly increases computation time.

NGAS1 : Flag for gaseous species (excluding H_2O) to be included in transport calculations.
> = 0 Gases (other than H_2O and CO2 in EOS2 or ECO2n) are not transported.
> ≥ 1 Gas species are included in transport calculations (besides H_2O and CO2 in EOS2 or ECO2n), unless fixed individually in chemical.inp

ICHDUMP : flag to enable detailed printout of chemical speciation results (typically enabled only for debugging chemical convergence problems).
> 0 Disabled
> 1 Printout of chemical speciation at each grid block and each time step
> 2 Printout of chemical speciation at time intervals specified by NWTI in the following Record_7 and grid blocks specified in Record_8.
> If this option is enabled, the program will abort after the output of speciation results for the first 1000 grid blocks and/or time steps, to avoid accidentally filling up disk space.

KCPL : flag to consider feedback effects of changes of porosity, permeability, and capillary pressure due to mineral dissolution and precipitation on flow.
> 0 Disabled
> 1 Enabled
> 2 Only monitor changes in output files, without feedback on flow.
> (To consider porosity changes from sedimentation, with option MOPR(11)=1, this flag must be set ≥ 1)

ICO2H2O : flag to consider effects of CO_2 and/or H_2O reaction source/sink terms on fluid flow calculations. ICO2H2O can be used for H_2O reaction source/sink terms in all EOS modules, however, CO_2 and H_2O are only possible using the EOS2 and ECO2N EOS modules. .
> 0 Effects ignored
> 1 Only effects of CO_2 reaction source/sink terms
> 2 Effects of both CO_2 and H_2O reaction source/sink terms

iTDS_REACT : Must be set to zero in this version (not used)

Record_3. Options for reactive geochemical transport (2)

Variable: SL1MIN, RCOUR, STIMAX, CNFACT

Format: Real (free format)

SL1MIN: Geochemical calculations are skipped at grid blocks where the liquid saturation is less than SL1MIN. For typical boiling simulations, use SL1MIN less than or equal to 10^{-3}.

RCOUR : both a variable and a flag to limit the time step size. RCOUR ≠ 0.0 limits the maximum time step size to |RCOUR| × Courant Number. Positive RCOUR values limit the time step by the velocity of the gas or liquid phase, whichever is highest. Negative RCOUR values limit the time step by the velocity of the liquid phase only. This option is disabled if RCOUR = 0.0.

STIMAX : Geochemical calculations are skipped at grid blocks where the stoichiometric ionic strength is more than STIMAX. STIMAX can be up to 6 mol/kg H_2O for NaCl-dominant solutions. For other solutions, STIMAX can be up to a value between 2.0 and 4.0 regarding the calculation of activity coefficients at elevated ionic strengths (see Appendix H for details).

CNFACT : Weighting factor for mineral and gas reaction source terms in the transport equations (1.0 = fully implicit source terms, 0.0 = fully explicit source terms). This parameter has an effect only if sequential iterations are enabled (ISPIA = 0). In this program version, CNFACT always defaults to 1.0 if a non-zero value is input (implicit only). Simulations with CNFACT = 0.0 using sequential iterations will produce the same results as simulations without sequential iterations (explicit source terms) but requires increased computing time and therefore should be avoided.

Record_4.1 through 4.6. Names of input thermodynamic database and output files regarding chemical data and numerical iterations

Variable: THERMO_in , OUTiter, OUTplot, OUTsolid, OUTgas, OUTtime

Format: A20, each file name occupies one line.

THERMO_in : name of thermodynamic data input file.

OUTiter   : name of file (e.g., iter.out) to output iteration information.

OUTplot   : name of file (e.g., aqconc.tec) to output aqueous concentrations in tecplot format for all grid blocks at specified printout times defined in flow.inp.

OUTsolid : name of file (e.g., minerals.tec) to output mineral abundances and exchanged species concentrations in tecplot format for all grid blocks at specified printout times defined in flow.inp.

OUTgas : name of file (e.g., gases.tec) to output gas pressures in tecplot format for all grid blocks at specified times defined in flow.inp.

OUTtime : name of file (e.g., time.out) to output aqueous concentrations, mineral/gas abundances, and adsorbed/exchanged species concentrations versus time, in tecplot format, for specific grid blocks input in Record_8, at time step intervals (NWTI) input in Record_7.

Record_5. Weighting parameters and diffusion coefficients

Variable: WTIME, WUPC, DIFUN, DIFUNG

Format: 4F (real free format)

WTIME : time weighting factor, ranging from 0.0 to 1.0. WTIME = 1.0 (implicit) is recommended.

WUPC : upstream weighting factor, ranging from 0.0 to 1.0. WUPC = 1.0 (fully upstream) is recommended.

DIFUN   : diffusion coefficient (m^2/s) for aqueous species. DIFUN is multiplied by the tortuosity (τ) (defined in the ROCKS block of the flow input file, flow.inp), porosity, and liquid saturation. Notice that if τ in flow input is zero, the program computes τ from $\tau_\beta = \phi^{1/3} S_\beta^{7/3}$ (Millington and Quirk, 1961), where ϕ is porosity, S is phase saturation, and β is the fluid phase index.

DIFUNG : diffusion coefficients (m^2/s) of the medium for gaseous species other than H_2O. If DIFUNG < 0.0, TOUGHREACT computes gaseous diffusion coefficients as function of molecular weight and diameter, temperature, and pressure according to Eq. A.1 (Appendix A). DIFUNG is multiplied by the tortuosity (τ), defined in the ROCKS block of the flow input (flow.inp), porosity, and gas saturation, or if τ=0.0, the Millington-Quirk formulation is used as described for aqueous diffusion coefficients.

Record_6. Data related to convergence criteria

Variable: MAXITPTR, TOLTR, MAXITPCH, TOLCH, MAXITPAD, TOLAD, TOLDC, TOLDR

Format: I, E, I, E, I, E, E, E (All are free format)

MAXITPTR: maximum number of sequential iterations between transport and chemistry. If MAXITPTR=1, a sequential non-iterative approach is used where transport and chemistry are sequentially solved without iteration. Note that the value of MAXITPTR has no effect if ISPIA in Record_2 is set to 2 (non-iterative approach). Computing performance will significantly decrease as MAXITPTR increases.

TOLTR: convergence criterion (as relative change of aqueous concentrations) for the sequential iterative (transport/chemistry) scheme; a value between 1.0E-03 to 1.0E-06 is suggested. This convergence criterion is used only when MAXITPTR > 1 and ISPIA=0.

MAXITPCH: maximum number of iterations allowed for solving chemical speciation.   In most cases, a value of 300 is appropriate.

TOLCH: convergence criterion (as relative change of aqueous concentrations) for chemical speciation computations; a value between 1.0E-05 to 1.0E-07 is suggested. For simulations with a large number of time steps (> 10,000), values larger than 1.0E-6 should be avoided to minimize the potential for cumulative mass balance errors.

MAXITPAD: not currently used.

TOLAD: not currently used.

TOLDC: relative concentration change (between two consecutive time steps) tolerance for quasi-stationary state (QSS); a value between 1.0E-03 to 1.0E-06 is suggested; if not using the QSS option, set equal to zero. MOPR(4) (in flow.inp) must be set to 1 to enable this option. When KCPL>0 or ICO2H2O>0 or iTDS_REACT in Record_2, no QSS can be attained and this option is not available, set equal to zero.

TOLDR: relative dissolution and/or precipitation rate change tolerance for the quasi-stationary state option (QSS) (i.e., if TOLDC ≠ 0); a value between 1.0E-03 to 1.0E-06 is suggested; if not using QSS approximation set equal to zero. When KCPL>0 or ICO2H2O>0 or iTDS_REACT in Record_2, set equal to zero.

Record_7. Output control variables

Variable: NWTI, NWNOD, NWCOM, NWMIN, NWAQ, NWADS, NWEXC, ICONFLAG, MINFLAG, IGASFLAG

Format: 10I (integer free format)

NWTI : printout frequency (i.e., every NWTI time steps) of model output for selected grid blocks (NWNOD≠0). These data will be output in the file specified on Record_4.6. NWTI also controls the printout frequency in the iteration file (Record 4.2), after the first 20 time steps are written. If NWTI is negative, then all time steps are written in the iteration file but NWTI are written for the selected grid blocks in the time evolution file.

NWNOD : number of grid blocks for time evolution printout. NWNOD grid blocks (with names EL) will be read below on Record_8. NWNOD can be set to a negative value as a flag for line-by-line input starting on Record_8.

NWCOM : number of chemical components (species) for which to output total concentrations in files specified on Record_4.3 and Record_4.6. NWCOM primary species (with indices IWCOM) will be read below on Record_9. If NWCOM is set to 0, and IWCOM(1) lists only 0, then all chemical components will be written out. NWCOM can also be set to a negative value, in which case species names (instead of indices) will be read line-by-line starting on Record_9.

NWMIN : number of minerals for which to output abundances in files specified on Record_4.4 and Record_4.6. NWMIN minerals (with indices IWMIN) will be read below in Record_10. If NWMIN is set to 0, and IWMIN(1) lists only 0, then all minerals will be written out. NWMIN can also be set to a negative value, in which case mineral names (instead of indices) will be read line-by-line starting on Record_10.

NWAQ : number of individual aqueous species for which to output concentrations in files specified on Record_4.3 and Record_4.6. NWAQ species (with indices IWAQ) will be read below in Record_11. NWAQ can be set to a negative value, in which case species names (instead of indices) will be read line-by-line starting on Record_11.

NWADS : number of surface complexes for which to output concentrations in files specified on Record_4.3 and Record_4.6. NWADS surface complexes (with indices IWADS) will be read below in Record_12. NWADS can be set to a negative value, in which case names of surface complexes (instead of indices) will be read line-by-line starting on Record_12.

NWEXC : number of exchange species for which to output concentrations in files specified on Record_4.3 and Record_4.6. NWEXC exchange species (with indices IWEXC) will be read below in Record_13. NWEXC can be set to a negative value, in which case names of exchange species (instead of indices) will be read line-by-line starting on Record_13.

ICONFLAG: flag to specify the aqueous concentration units in output files specified on Record_4.3 and Record_4.6.
  =0 mol/kg H_2O (molal)
  =1 mol/L liquid (molar – concentrations will change as water density changes with temperature!)
  =2 g/L liquid (concentrations will change as water density changes with temperature!)
  =3 mg/L (~ppm if water density remains close to 1 g/cc; concentrations will change as water density changes with temperature!)

MINFLAG: flag for units of mineral abundances output in files specified on Record_4.4 and Record_4.6.
  =0 Change (relative to t = 0) of mineral abundance in mol/m3 medium
  =1 Change (relative to t = 0) of mineral abundance in volume fraction (dimensionless)
  =2   Current mineral abundance (total amount) in volume fraction (dimensionless)
  =3   Change (relative to t = 0) of mineral abundance in volume %

IGASFLAG: flag for units of gas concentration output in files specified on Record_4.5 and Record_4.6.

> =0   Partial pressure (bars)
>
> =1   Mole fraction (equivalent to volume fraction for ideal gas)

Record_8.   List of grid blocks for printout of time evolution results

If NWNOD (on Record_7) > 0:

> Variable: EL(I), I=1,NWNOD
>
> Format: 15A5
>
> Description: five-character code name of a grid block (up to 200 names, 15 per record). NWNOD names will be read. Each name must match one of those specified in the flow.inp input file or MESH file. No blank line follows the list!

If NWNOD (on Record_7) < 0:

> Variable: EL(I), I=1,N
>
> Format: A5
>
> Description: Five-character code name of a grid block (up to 200, one name per record). The list of names must end with a blank record. Each name must match one of those specified in the flow.inp input file or MESH file.

If NWNOD (on Record_7) =0: leave a blank record.

Record_9.   Indices or names of component species for which to output total concentrations

If NWCOM (on Record_7) >= 0:

> Variable: IWCOM(I), I=1,NWCOM
>
> Format: Integer (free format). One record up to 200 characters long. NWCOM indices will be read, up to total number of primary species. If NWCOM = 0 and IWCOM(1) = 0, then all species will be written out. No blank line follows this record!

Description: indices of component species.

If NWCOM (on Record_7) <0:

> Variable: PRT_COM(I), I=1,N
>
> Format: A20 (one name per record, without quotes, up to total number of primary species). The list of names must end with a blank record. Each name must match one of those specified in the thermodynamic database and included in the simulation (e.g. in file chemical.inp).

Description: names of component species

If NWCOM (on Record_7) =0: leave a blank record.

Record_10. Indices or names of minerals for which to output amounts

If NWMIN (on Record_7) >= 0:

      Variable: (IWMIN(I), I=1, NWMIN)

      Format: Integer (free format). One record up to 200 characters long. NWMIN indices will be read, up to total number of minerals.   If NWMIN = 0 and IWMIN(1) = 0, then all minerals will be written out. No blank line follows this record!

   Description: indices of minerals (which correspond to order entered in chemical.inp)

If NWMIN (on Record_7) <0:

      Variable: PRT_MIN(I), I=1,N

      Format: A20 (one name per record, without quotes, up to total number of minerals). The list of names must end with a blank record. Each name must match one of those specified in the thermodynamic database and included in the simulation (e.g. in file chemical.inp).

   Description: names of minerals

If NWMIN=0 (on Record_7): leave a blank record.

Record_11. Indices or names of individual aqueous species for which to output concentrations

If NWAQ (on Record_7) > 0:

      Variable: (IWAQ(I), I=1, NWAQ)

      Format: Integer (free format). One record, up to 200 characters long. NWAQ indices will be read, up to total number of individual species. No blank line follows this record!

   Description: indices of aqueous species (e.g., as shown in chemical.inp)

If NWAQ (on Record_7) <0:

      Variable: PRT_AQ(I), I=1,N

      Format: A20 (one name per record, without quotes, up to total number of individual species). The list of names must end with a blank record. Each name must match one of those specified in the thermodynamic database and included in the simulation (e.g. in file chemical.inp).

   Description: names of aqueous species

If NWAQ=0 (on Record_7): leave a blank record.

Record_12. Indices or names of surface complexes for which to output concentrations

If NWADS (on Record_7) > 0:

> Variable: (IWADS(I), I=1, NWADS)

> Format: Integer (free format). One record up to 200 characters long. NWADS indices will be read, up to total number of surface complexes. No blank line follows this record!

Description: indices of surface complexes (e.g., as shown in chemical.inp)

If NWADS (on Record_7) <0:

> Variable: PRT_ADS(I), I=1,N

> Format: A20 (one name per record, without quotes, up to total number of surface complexes). The list of names must end with a blank record. Each name must match one of those specified in the thermodynamic database and included in the simulation (e.g. in file chemical.inp).

Description: names of surface complexes

If NWADS=0 (on Record_7): leave a blank record.

Record_13. Indices or names of exchange species for which to output concentrations

If NWEXC (on Record_7) > 0:

> Variable: (IWEXC(I), I=1, NWEXC)

> Format: Integer (free format). One record up to 200 characters long. NWEXC indices will be read, up to total number of exchange species. No blank line follows this record!

Description: indices of exchange species (e.g., as shown in chemical.inp)

If NWEXC (on Record_7) <0:

> Variable: PRT_EXC(I), I=1,N

> Format: A20 (one name per record, without quotes, up to total number of exchange species). The list of names must end with a blank record. Each name must match one of those specified in the simulation (e.g. in file chemical.inp).

Description: names of exchange species

If NWEXC=0 (on Record_7): leave a blank record.

Record_14. Default indices for all chemical property zones

If MOPR(11) ≠ 1 (in flow.inp)

> Variable: IZIWDF, IZBWDF,IZMIDF,IZGSDF, IZADDF,IZEXDF, IZPPDF,IZKDDF, IZBGDF

Format: 9I (integer free format)

Description: IZIWDF, IZBWDF, IZMIDF, IZGSDF, IZADDF, IZEXDF, IZPPDF, IZKDDF, and IZBGDF are default values of IZIW, IZBW, IZMI, IZGS, IZAD, IZEX, IZPP, IZKD, and IZBG, respectively, as described for Record_15.

If MOPR(11) = 1 (in flow.inp)

Variable: IZIWDF, IZBWDF, IZMIDF, IZGSDF, IZADDF, IZEXDF, IZPPDF, IZKDDF, IZBGDF, VSED

Format: 9I, F (free format)

Description: Same as above, except for the last variable, VSED, which is the sedimentation velocity (m/s). This option will only work for a vertical 1D column with grid blocks and connections sequentially ordered from top to bottom.

Record_15. Chemical property zone indices for specific grid blocks

If MOPR(11) ≠ 1 (in flow.inp)

Variable: EL, NSEQ, NADD, IZIW, IZBW, IZMI, IZGS, IZAD, IZEX, IZPP, IZKD, IZBG

Format: A5,11I (integer free format), one record per grid block, up to the total number of grid blocks. The list of records must end with a blank record.

EL: grid block name

NSEQ: number of additional grid blocks having the same chemical properties

NADD: increment between the code numbers of two successive grid blocks

Indices of the various zones (for different waters, mineralogies, gas compositions, sorption characteristics, etc.) defined in file chemical.inp:

IZIW: initial water zone number

IZBW: injection (boundary) water zone number

IZMI: mineral zone number

IZGS: gas zone number

IZAD: adsorption zone number

IZEX: ion exchange zone number

IZPP: zone number for porosity-permeability relation

IZKD: linear adsorption Kd zone number

IZBG: injection (boundary) gas zone number

If MOPR(11) = 1 (in flow.inp)

Variable: EL, NSEQ, NADD, IZIW, IZBW, IZMI, IZGS, IZAD, IZEX, IZPP, IZKD, IZBG, VSED

Format: A5, 11I, F (free integer and real format) one record per grid block, up to the total number of grid blocks. The list of records must end with a blank record.

Description: Same as above, except for the last variable, VSED, which is the sedimentation velocity (m/s). This option will only work for a vertical 1D column with grid blocks and connections sequentially ordered from top to bottom. By specifying decreasing velocities with depth, the effect of compaction can be approximated (set KCPL > 0 in Record_2 to capture resulting porosity changes).

6.3   Geochemical Input (chemical.inp)

All variables in this file are input in free format. Input character variables must be enclosed in quotes, and variables that are not used must be entered as zero values and cannot be left blank, unless specifically indicated otherwise.

Inputs are organized in groups (e.g., records Akin for aqueous kinetics, Aque for aqueous species, Mine for minerals, etc.). These groups are always preceded by a header record, and always end with a trailing record starting with '*' (or a blank record). Entries for any group can be skipped altogether (e.g., if no minerals are present), however one or more "skip" records followed by a trailing ('*') record must always be entered in the file for all groups. The order in which input groups are entered cannot be changed from that shown below.

Names of all aqueous species, gases, and minerals input in this file are internally converted to lower case characters. The electronic charge in the names of cations and anions are also internally converted to display the charge sign followed by the number of charges (for example, 'CO3--' is converted to 'co3-2' and 'Al+++' is converted to 'al+3'. This allows for input flexibility and maintains internal consistency. Examples of chemical.inp are given in Figure 8.1-4, 8.2-2, 8.9-4 and 8.10-5.

"Skip" records:

One or more heading (comment) line can precede each record described below (see inputs of the sample problems, such as in Figure 8.2-2). The comment line is indicated by beginning with "#" followed by one blank (without quotes), or any blank record, and will be skipped on input. These "skip" records can be inserted anywhere in the file, except within input blocks that end with '*'. These "skip" records can be also used for data source references, or other purpose.

Record-1. Title

Variable: TITLE

Format: A (free format)

TITLE: title and comments in one line.

Record-2. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments to appear in the output file.

6.3.1 Definition of the geochemical system

These records contain the information on aqueous species, minerals, gases, surface complexes, species with linear adsorption Kd and radioactive decay, and exchangeable cations. Their names must match exactly those in the thermodynamic database file (it's not case sensitive).

Record-3. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments to appear in the output file.

Primary species (Prim)

Prim-1. Header for Prim records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Prim records.

Prim-2. Primary aqueous species

Variable: NAPRI, NOTRANS, NAADS_MIN, SDENS, IMOD, CAPAC

Format: A, I, A, F, I, F (free format, one record per primary species)

NAPRI: name of the primary species, enclosed in quotes (truncated after 20 characters). It must match exactly that in the thermodynamic database file. A record starting with '*' is needed to indicate the end of the list of the primary species.

NOTRANS: flag for transport and surface complexation options.

=0   species (component) will be transported

=1   no transport for this species (component)

All species specified with NOTRANS ≥2 must be listed at the end of the list of species.

=2   flag to indicate this is a surface (primary) species, with molality-based surface complexation constants in the thermodynamic database.

=3   flag to indicate this is a surface (primary) species, with mole-fraction based surface complexation constants in the thermodynamic database.

=4   flag to indicate this is a surface (primary) species, with equivalent-fraction based surface complexation constants in the thermodynamic database (e.g., as with phreeqc v2).

The remaining variables on record Prim-2 are required only if NOTRANS=2

NAADS_MIN: name of mineral associated with this surface species (in quotes, up to 20 characters). More than one surface species (NAPRI) can be associated with the same mineral. NAADS_MIN can be either:

A name (in quotes) matching the name of one of the minerals included in the simulation (on record Mine-1), or

'no_mineral' (including quotes), in this case sorption is not tied to a specific mineral, and a constant sorption surface area is entered in $cm^2/g_{mineral}$ on record Zads-6, or

'surface.....' (including quotes; the first 7 characters after the initial quote must spell *surface*): in this case adsorption is tied to a generic surface with a constant sorption surface area input in m^2/kg_{H2O} on record Zads-6.

SDENS: sorption site density in $mol_{sites}/m^2_{mineral}$ for this surface species

IMOD: adsorption model type.

=0 surface complexation without electrostatic terms

=1 constant capacitance model

=2 double diffuse layer model, linear

=3 double diffuse layer model, Gouy-Chapman (most common)

CAPAC: this variable must be entered only if IMOD=1. Capacitance in $F\ m^{-2}$ (these units are identical to $C\ V^{-1}\ m^{-2}$)

Prim-3. Trailer for Prim records

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

Aqueous Kinetics (Akin)

Akin-1: Header for Akin records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL : character string starting with 'AQUEOUS KINETICS' (including quotes; upper or lower case.

Akin-2:

Variable: NTRX

Format: I (free format)

NTRX : Total number of kinetic reactions among aqueous species

The following records, from Akin-3 through Akin-9, are repeated NTRX times. The format of this input block is given below.

Akin-3:

Variable: IRX

Format: I (free format)

IRX : Index of kinetic reaction, from 1 to NTRX.

Akin-4:

Variable: NCP, (S(i), NAM(i), I = 1, NCP), irkaq_typ, rkaq_logK, rkaq_cf

Format: I, NCP(F, A), I, 2F (free format)

NCP : number of aqueous species involved in each reaction

S : stoichiometric coefficients of primary species NAM included in the reaction. Negative values are for reactants, positive values for products. The stoichiometric coefficients must be in terms of moles for the species involving in other reactions such as aqueous complexation, cation exchange and mineral dissolution and precipitation (undergoing mass-action calculations). Otherwise, they can be input in any units such as mg and g. Details are illustrated in the related sample problems (in Sections 8.9 and 8.10).

The last three entries below are optional and are used to define a reaction affinity term to limit, stop, and potentially reverse the rate of the reaction as it reaches and potentially crosses the equilibrium point. The affinity term is based on the reaction ion activity product Q and the

reaction equilibrium constant *K*.   Note that *Q/K* is always positive and equals 1 at equilibrium. When *Q/K* is < 1 and the specified reaction rate (RKAQ) is positive, the reaction proceeds from left to right (the "normal" case). If *Q/K* > 1 (with a positive RKAQ), the reaction can reverse and proceeds from right to left.

irkaq_typ: if not zero nor blank, this flag enables limiting the reaction rate by an affinity term (fG) that multiplies the reaction rate and drops to zero at equilibrium. The form of the affinity term depends on the value of irkaq_typ, as shown below.

=0 f_G = 1 (no limit – beware, the equilibrium point may be overshot!)

=1   Function based on transition state theory (TST):

$f_G = (1 - Q/K)^{rkaq\_cf}$ (f_G varies from +1 to 0 when reaction is from left to right)
(f_G varies from 0 to large numbers when reaction is from right to left)

Note that primary species defined with NOTRANS=1 in record Prim-2 (see Section 6.3.1) are not included in the calculation of *Q*. When *Q/K* ≤ 1, the reaction proceeds from left to right, and f_G varies from 1 away from equilibrium to 0 at equilibrium (positive rate). When *Q/K* > 1, the reaction reverses (proceeds from right to left, i.e., negative rate) and f_G can become very large. Note that setting the coefficient *rkaq_cf* to a small value limits the upper value of f_G and can help convergence.

=2   Symmetric TST form with f_G varying between +1 and –1:
$f_G = (1 - Q/K)^{rkaq\_cf}$ when *Q/K* ≤ 1 (f_G varies from +1 to 0; reaction from left to right)
$f_G = - (1 - K/Q)^{rkaq\_cf}$ when *Q/K* ≥ 1 (f_G varies from 0 to – 1; reaction from right to left)

This option is useful in limiting the rate by the same amount on each side of the equilibrium point. It has no real theoretical basis.

=3   Similar effect as with irkaq_typ=2, with f_G varying between +1 and –1, but using a different function shape:

$$f_G = \frac{\log(\frac{Q}{K})}{|\log(\frac{Q}{K})| + rkaq\_cf}$$

Here the value of *rkaq_cf* is the value of log(*Q/K*) at which the rate is cut in half (i.e., at which f_G = ±0.5). This function has no real theoretical basis.

=4   Same effect as irkaq=1 in the forward direction (TST affinity term when reaction operates from left to right), but reversal of the reaction is not allowed (i.e., f_G = 0 in the reverse direction).

rkaq_cf: value of coefficient *c* in the affinity functions described above.

rkaq_logK: log of the equilibrium constant *K* of the reaction.

Akin-5:

Variable: I_MOD, N_MECH

Format: 2I (free format)

I_MOD : Type-index of kinetic rate model.

=1 Main model currently implemented (Eq. B.2 in Appendix B)

=2 Not used (do not use as it may create an input error)

=3 Special case: Monod and inhibition limiters in Eq. B.2 are suppressed when the reaction operates in a reverse direction (i.e., when f_G becomes negative, the rate is not multiplied by Monod and inhibition terms).

N_MECH : Number of mechanisms (pathways) to include in the rate expression.

Akin-6:

Variable: RKAQ

Format: F (free format)

RKAQ : forward rate constant or maximum specific growth rate (mass/L/s). If RKAQ = -1.0, the rate constant will be temperature-dependent, and dynamically calculated according to the following equation:

$$k = k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15} \right) \right]$$

Where E_{25} is a rate constant (1/s) at 25°C, and E_a is activation energy (KJ/mol), and T is the absolute temperature. E_{25} and E_a need to read from additional record AKIN-6-1

Akin-6-1:

Variable: RK_a, RK_b

Format: F, F (free format)

RK_a : is k_{25} of the above equation (1/s).

RK_b : is E_a of the above equation (KJ/mol).

Akin-7:

Variable: NCP_rx1, (NAM_rx1(i), ia1(i), S_rx1(i), i=1,NCP_rx1)

Format: F, NCP_rx1(A, I, F) (free format)

NCP_rx1 : Number of species (primary or secondary) involved in product terms, see Eq. B.2 in Appendix B

NAM_rx1 : chemical formula of the species.

ia1: flag for using activity (ia1 = 1) or concentration (ia1 = 2) of the species for calculations of the product term

S_rx1 : value of power term applied to activity or concentration of the species

Akin-8:

Variable: NCP_rx2, (NAM_rx2(i), ia2(i), S_rx2(i), i=1,NCP_rx2)

Format: F, NCP_rx2(A, I, F) (free format)

NCP_rx2 : Number of species (primary or secondary) involved in Monod terms, see Eq. B.2 in Appendix B

NAM_rx2 : chemical formula of the species.

Ia2: flag for using activity (ia1 = 1) or concentration (ia1 = 2) or total concentration (ia1 = 3, only for primary species) of the species for calculations of the Monod term

S_rx2 : value of half-saturation constant for the species

Akin-9:

Variable: NCP_rx3, (NAM_rx3(i), ia3(i), S_rx3(i), i=1,NCP_rx3)

Format: F, NCP_rx3(A, I, F) (free format)

NCP_rx3 : Number of species (primary or secondary) involved in Inhibition terms, see Eq. B.2 in Appendix B

NAM_rx3 : chemical formula of the species.

Ia3: flag for using activity (ia1 = 1) or concentration (ia1 = 2) or total concentration (ia1 = 3, only for primary species) of the species for calculations of the inhibition term

S_rx3 : value of inhibition constant for the species

Akin-10: Trailer for Akin records

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

Secondary aqueous species (Aque)

Aque-1. Header for Aque records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Aque records.

Aque-2. Secondary aqueous species

This input block can be omitted. In this case, all possible secondary aqueous species found in the input thermodynamic database will be automatically selected.

Variable: NAAQX

Format: A (free format, one record per secondary species)

NAAQX: name of secondary aqueous species, in quotes (truncated after 20 characters). The name must match exactly that in the thermodynamic database file.

Aque-3. Trailer for Aque records

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

Minerals (Miner)

Miner-1. Header for Miner records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Aque records.

The following two main records (Miner-2 and Miner-3) are repeated as many times as the number of minerals. Minerals can be entered in any order as long as the minerals at equilibrium precede those under kinetic constraints. The specified minerals consist of reactants and any possible products. Their names must match exactly the names of minerals in the database. Minerals with identical stoichiometries (e.g., quartz and cristobalite) cannot both be specified at equilibrium, but can be specified to react under kinetic constraints. Minerals under kinetic constraints require more records (per mineral) than minerals under equilibrium constraints.

Miner-2.

Variable: NAMIN, IKIN, IDISPRE, ISS, M1

Format: A, 4I (free format)

NAMIN: name of the mineral phase, in quotes (truncated after 20 characters). It must be consistent with that in the thermodynamic database. Omit NAMIN if no minerals are

required. However, the trailer record starting with '*' (or blank) is always needed to indicate the end of the list.

IKIN: flag for the type of mineral: 0 for minerals at equilibrium, and 1 for those under kinetic constraints.

IDISPRE: flag for the type of kinetic constraint: 1 for dissolution only, 2 for precipitation only, and 3 for both (mineral can either precipitate or dissolve). Always set IDISPRE = 0 if IKIN = 0; and IDISPRE > 0 if IKIN = 1.

ISS: index for a solid solution mineral endmember. All endmembers for a specified phase are given the same ISS value: ISS = 1 for each endmember of the first solid solution, ISS = 2 for each endmember of the second solid solution, and so on (numbers cannot be skipped). Records for each member can appear in any order in the mineral records.

M1: flag to indicate that the mineral may precipitate in a dry grid block as a result of complete evaporation (when liquid saturation < sl1min specified in the solute.inp file), or if there is water flux into the grid block that dries out during the flow step (and therefore liquid saturation is zero). The mineral with M1 = 1 precipitates first, with M1 = 2 second, and so on. If this flag is set to zero, then the mineral will not be formed in the dry grid block.

If IKIN = 1 and IDSPRE = 1 or 3, one or more additional records (Miner-2.1) are required to define dissolution rate law parameters.

If IKIN = 1 and IDSPRE = 2 or 3, one or more additional records (Miner-2.2) are required to define precipitation rate law parameters.

Miner-2.1.

Variable: RKF, IDEP, CK1, CK2, EA, ACFDISS, BCFDISS, CCFDISS

Format: F, I, 6F (free format)

RKF: coefficient k_{25} in the expression (B.7) given in Appendix B, where k_{25} is the rate constant (in mol/m^2/sec) at 25°C, EA is the activation energy in kJ/mol. The form of the rate law is given in Eq. (B.6).

IDEP: flag for rate constant dependence on pH (see Figure B.4-1 in Appendix B) or multiple mechanisms (see Eq. B.13 in Appendix B). If IDEP = 0, pH (species) dependent rate constants and multiple mechanisms are not considered. If IDEP = 1, and additional record (Miner-2.1.1) must be entered to include information on the rate dependence on pH. If IDEP = 2, additional records Miner-2.1.2 and Miner-2.1.2.1 must be entered to include information on the rate constants contributed from additional mechanisms.

CK1 and CK2: the exponents η and θ, respectively in Eq. (B.6).

EA: the activation energy (kJ/mol).

ACFDISS, BCFDISS, and CCFDISS: should be set to zero, unless a different form of rate constant dependence with temperature is desired. This alternate form is: $\log_{10}(k) = a + b \cdot T + c/T$, where T is absolute temperature in K. To enable this option, RFK must be set to 1.0, EA must be set to 0.0, CK1 and CK2 can be set to any value, and ACFDISS, BCFDISS, and CCFDISS must be specified as the coefficients a, b, and c, respectively, in the above expression.

Miner-2.1.1 (only if IDEP = 1)

> Variable: PH1, SLOPE1, PH2, SLOPE2

> Format: 4F (free format)

> See Figure B.4-1 (in Appendix B) for the meaning of these parameters.

Miner-2.1.2 (only if IDEP = 2)

> Variable: NDIS

> Format: I (free format)

> > NDIS is the number of additional mechanisms contributed to the rate constant (see Eq. B. 13 in Appendix B) (maximum allowed is 5). An example of the multiple mechanisms can be found in the CO_2 disposal sample problem (Section 8.5).

Miner-2.1.2.1 (repeat NDIS times after Miner-2.1.2, only if IDEP=2)

> Variable: RKDS, EADS, NSPDS, NADIS, EXPDSP

> Format: 2F, I, A, F (free format)

> > RKDS is k_i in Eq. (B. 13) where i is the additional mechanism index.

> > EADS: is the activation energy (kJ/mol) for each additional mechanism.

> > NSPDS: is the number of species involved in each mechanism (a maximum of five species can be considered).

> > NADIS is the name of species involved in the mechanism that must be in the list of primary or secondary species. NADIS and the following variable EXPDSP must be repeated as many as NSPDS times.

> > EXPDSP is the power term n_j in Eq. (B. 13).

Miner-2.2.

> > Variable: RKPREC, IDEPREC, CK1PREC, CK2PREC, EAPREC, ACFPREC, BCFPREC, CCFPREC, RNUCL, NPLAW

> > Format: F, I, 7F, I (free formats)

> > The first 8 input parameters are listed in the same order and have the same functions as those described above for mineral dissolution, except that the parameters apply to mineral precipitation instead of dissolution. Therefore if IDEPREC = 1, an additional record identical to Miner-2.1.1 needs to include information on the rate dependence on pH; if IDEPREC = 2, additional records identical to Miner-2.1.2 and Miner-2.1.2.1 need to be inserted with information on the rate constants contributed from additional mechanisms.

> > RNUCL: the initial volume fraction ($V_{mineral}/V_{solid}$) to be assumed for calculating initial effective surface area if the mineral is not present at the start of a simulation but precipitates as a new reaction product. If zero, RNUCL is assumed to be 10^{-15}.

NPLAW: precipitation law index. NPLAW = 0 for Eq. (B.6 and B.13) in Appendix B; NPLAW = 1 for Eq. (B.9).

Miner-3.

This record is required for all minerals reacting at equilibrium, but only for those minerals reacting under kinetic constraints that are allowed to precipitate (IDSPRE = 2 or 3).

Variable: SSQK0, SSTK1, SSTK2

Format: 3F (free format)

SSQK0: log (Q/K) gap (supersaturation window, see Eq, B.14 in Appendix B). A zero value represents no gap.

SSTK1: temperature (in °C) at which to begin reducing gap.

SSTK2: temperature (in °C) endpoint at which the gap has diminished to nearly zero (1% of original value). The gap decreases exponentially from the first (SSTK1) to the second (SSTK2) temperature, and SSTK2 must always be greater than SSTK1.

Miner-4. Trailer for Mine records

Variable: LABEL

Format: A (free format)

Gaseous species (Gas)

Note that H2O gas should not be entered in the list of gases here, because H_2O transport and thermodynamics are always treated by the TOUGH2 EOS modules. TOUGHREACT V3.0-OMP has two new capabilities/options: (1) Trace gas species transport in multiphase EOS modules having other "carrier" gases such as CO_2, (2) Option to fix individual gas species fugacities (IGASFIX).

Gas-1. Header for Gas records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Gas records.

Gas-2. Gases

Variable: NAGAS, IGASFIX

Format: A, I (free format, one record per gas)

NAGAS: name of a gaseous species, in quotes (truncated after 20 characters). It must match exactly that in the thermodynamic database file. Omit NAGAS if no gaseous species are

required. However, the trailer record starting with '*' (or blank) is always needed to indicate the end of the list.

IGASFIX: flag to fix individual gas species fugacities

= 0 Gas species fugacity allowed to change according to reactive-transport calculations

= 1 Fix gas species fugacity based on value assigned in gas zone or calculated from initial water composition

Gas-3. Trailer for Gas records

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

Surface complexes (Surx)

Surx-1. Header for Surx records (a "Skip" record)

Variable: LABEL

 Format: A (free format)

LABEL: header describing Surx records.

Surx-2. Surface complexes

This input block can be omitted. In this case, all possible surface complexes found in the input thermodynamic database will be automatically selected.

Variable: NAADS

Format: A (free format, one record per surface complex)

NAADS: name of surface complex, in quotes (truncated after 20 characters). Omit NAADS if no surface complexes are required. However, the trailing record starting with '*' (or blank) is always needed to indicate the end of the list.

Surx-3. Trailer for Surx records

Variable: LABEL

Format: A (free format)

LABEL: header describing Kdde records.

Aqueous species (primary) with Kd and decay (Kdde)

Kdde-1. Header for Kdde records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Kdde records.

Kdde-2. Species with Kd and decay

Variable: NAKDD, DECAYC, a_TDecay, b_TDecay

Format: A, F, F, F (free format, one species per record)

NAKDD: name of the aqueous primary species with Kd and/or decay, in quotes (truncated after 20 characters). These names must appear in the above mentioned primary species records (Prim records). Omit these records if no primary species with Kd and/or decay are required. However, the trailing record starting with '*' (or blank) is always needed to indicate the end of the list.

DECAYC: a positive value is radioactive decay constant (in 1/s). For species with only Kd adsorption and without decay, set DECAYC equal to 0.0. For DECAYC greater than or equals to zero (0.0), set the following two parameters (a_TDecay and b_TDecay) to zero.   If DECAYC=-1.0, the decay constant is temperature-dependent according to $\ln(k) = a - b/T$ (ln stands for natural logarithm), where k is the decay constant (in **1/day**), a and b are two parameters that will read from the following two variables, and T is absolute temperature in K.

a_TDecay: parameter a in the above equation.

b_TDecay: parameter b in the above equation.

Kdde-3. Trailer for Kdde records

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

Exchanged species (Exch)

Exch-1. Header for Exch records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Exch records.

Exch-2. Number of exchange sites

Variable: NXsites, Mod_Xsl

Format: 2I (free format)

 NXsites: number of exchange sites

 Mod_Xsl: Models for dependence of exchange sites on water saturation. Mod_Xsl = 1 for ideal-wetting condition; Mod_Xsl = 2 for considers multiplying a (correction) factor f that depends on liquid saturation, $f(S_l)$. Details can be found in Appendix K.

Exch-3. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

 LABEL: sub-header describing the data that follows.

Exch-4. Exchanged species

Variable: NAEXC IMS IEX (EKX(i), i=1,NXsites)

Format: A, 2I, NXsites(F) (free format, one record per exchanged species)

 NAEXC: name of exchangeable species, in quotes (truncated after 20 characters). Omit NAEXC if no exchangeable cations are required. However, a record starting with '*' is always needed to indicate the end of the list.

 IMS: If IMS = 1, the cation is used as reference for the exchange reactions (normally Na^+). For the remaining cations, IMS must be 0.

 IEX: exchange convention type used in the calculations: 1= Gaines-Thomas; 2= Vanselow; 3= Gapon (see Section B.6 of Appendix B for definition)). The value of IEX must be the same for all the exchanged cations.

 EKX: exchange coefficient of the cation with respect to the reference cation. If IMS = 1, then EKX = 1.0. Note, for example, if Na^+ is selected as the reference cation, using Gaines-Thomas convention (commonly used), for Na-Ca exchange Ca^{2+} selectivity must be specified according to the following reaction, $Na^+ + 0.5Ca-X_2 = 0.5Ca^{2+} + Na-X$ where X represents cation exchange site (see Section B.6 of Appendix B and Table 8.2-2 of Sample 2 for details). Note also that there are NXsites values, exch for one exchange site)

Exch-5. Trailer for Exch records

Variable: LABEL

Format: A (free format)

 LABEL: character string starting with '*' (including quotes) or blank record

6.3.2   Composition of initial and injection (boundary) waters (Water)

This section describes the different water zones initially assigned to various parts of the modeled system. These zones are mapped to the numerical grid through variables defined on Record_14 and Record_15, respectively, in file solute.inp, as described further below.

Water-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

   LABEL: comments or blank line.

Water-2. Header for Water records (a "Skip" record)

Variable: LABEL

Format: A (free format)

   LABEL: header describing Water records.

Water-3. Total number of different water compositions in the system

Variable: NIWTYPE NBWTYPE

Format: 2 I (free format)

   NIWTYPE: total number of aqueous solutions initially present in the system, excluding waters at boundaries and pumping/injection grid blocks. These are referred to as "initial waters".

   NBWTYPE: total number of aqueous solutions in pumping/injection grid blocks. These are often referred to as "boundary waters", although they are not used to set values in large boundary grid blocks. Initial waters are used for this purpose.

Aqueous solution compositions

This part describes the input of "initial" and "boundary" water compositions. Records Water-4, Water-5, Water-6, and Water-7 form the ensemble of records necessary to input one water composition. These records must be repeated NIWTYPE times for initial waters, followed by NBWTYPE times for boundary waters. Note that "boundary water" records must always follow "initial water" records. Each water composition is given a specific index, which is then mapped onto the numerical grid through variables IZIWDF and IZIW (for initial waters) and IZIBDF and IZIB (for boundary waters) on Record_14 and Record_15, respectively, in file solute.inp.

For boundary waters, the flux of each chemical component at the boundary is calculated from the given composition (Water-6) multiplied by the water flux given under keyword block 'GENER' in the *flow.inp* file (or in the separate GENER file). For a negative water flux (such as pumping and discharge), a boundary solution composition is not used, because it is determined by the composition of the producing grid block.

Each "initial" and "boundary" water composition defined here undergoes initial speciation computations, with results output in file chdump.out.

Water-4. Identification of the aqueous solution

Variable: IWTYPE TC2 PT

Format: I, F, F (free format)

IWTYPE: Index of the solution. This index must correspond to one of the water zone indices specified on Record_14 and Record_15 in file solute.inp. The value of IWTYPE must start at 1 for the first initial water, then sequentially increase up to NIWTYPE; it is then set again to 1 for the first boundary water, then increases again sequentially up to NBWTYPE.

TC2: temperature of the solution (°C). Note that this temperature is used only for initial speciation calculations for this water, before the water composition is assigned to different grid blocks. The initial temperatures and pressures of grid blocks assigned to this water composition are defined in the INCON block of the flow.inp file, and are not necessarily the same as TC2.

PT: pressure of the solution (bar). This value can be omitted, in which case PT is assumed to be 1 bar. As for TC2, this pressure is used only for initial speciation calculations for this water, before the water composition is assigned to different grid blocks. If PT is zero, or is below the water-saturation pressure, it is recalculated as the water saturation pressure at temperature TC2.

Water-5. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: sub-header describing the data that follows.

Water-6. Composition of aqueous solution

Variable: NAPRI ICON CGUESS CTOT NAMEQ QKSAT

Format: A, I, F, F, A, F (free format, one per primary species)

NAPRI: name of the primary aqueous species, in quotes (truncated after 20 characters). The name of the species must match exactly those previously listed as primary species in the definition of the system, although the order may change. The trailing record (Water-7) must end the list of species.

ICON: flag indicating the type of constraint controlling the input concentration of the aqueous species:

ICON=1: input values of CTOT represent total amounts (in moles) for aqueous species, and total kilograms for liquid H_2O. Thus, to input total molalities, set CTOT = 1 for H_2O.

ICON=2: the total concentration of the species will be computed such that the saturation index ($\log(Q/K)$) of mineral or gas NAMEQ equals QKSAT at temperature and pressure TC2 and PT, respectively. Therefore, for equilibrium with a mineral, use this option with QKSAT = 0.0, and for equilibrium with a gas at a given fugacity, use this option with QKSAT = log(fugacity). With this option, input CTOT values are irrelevant and discarded.

ICON =3: input values of CTOT represent the known activity of the specific species (i.e., not total concentration) at temperature and pressure TC2 and PT, respectively. For example, to input a known pH value, use this option and set CTOT = 10^{-pH} for H^+ activity.

ICON=4: the total concentration of the species is adjusted to yield charge balance. Use only with a charged species. If convergence occurs, choose a species with an opposite charge. With this option, input CTOT values are irrelevant and discarded.

CGUESS: initial guess (trial) value for the concentration of the individual primary species (not total concentration), in moles/kg H_2O (molal) for species other than H_2O and in kg for H_2O. Input values of CGUESS do not affect results of speciation calculations, but could affect the number of chemical iterations required during initial speciation computations.

CTOT: if ICON=1, CTOT is total moles of aqueous species, and total amount (in kg) of liquid water for H_2O. Molalities are then internally computed as $CTOT_{i \neq H2O}/CTOT_{H2O}$. If ICON > 1, refer to the discussion of ICON above for the meaning of CTOT.

NAMEQ: name of mineral or gas (in quotes) to use with option ICON=2. Names must match exactly those previously listed as minerals or gases in the definition of the chemical system. If ICON≠2, this entry is ignored, but cannot be omitted and should be entered as one of more characters between single quotes (suggested ' ' or '*').

QKSAT: desired value of mineral log(Q/K) or gas log(fugacity) when option ICON=2 is used. For equilibrium with mineral NAMEQ use QKSAT=0.0, and for equilibrium with gas NAMEQ at a given fugacity use QKSAT = log(fugacity). If ICON≠2, this entry is ignored, but cannot be omitted and should be entered as a real number (suggested 0.0).

Water-7. Trailer for Water records (one record after each water)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.3.3   Initial mineral zones (Imin)

This section describes the mineral zones initially present in the system. These zones are mapped to the numerical grid through variables IZMIDF and IZMI on Record_14 and Record_15, respectively, in file solute.inp.

Imin-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments or blank line.

Imin-2. Header for Imin records (a "Skip" record)

Variable: LABEL

Format: A (free format)

    LABEL: header describing Imin records.

Imin-3.

Variable: NMTYPE

Format: I (free format)

    NMTYPE: Total number of mineral zones in the system.

The following records (Imin-4, Imin-5 and Imin-6, and Imin-7) define each mineral zone, and must be repeated NMTYPE times.

Imin-4.

Variable: IMTYPE

Format: I (free format)

    IMTYPE: Index of the mineral zone. It must be 1 for the first zone, increasing sequentially thereafter. This index must correspond to one of the mineral zone indices specified on Record_14 and Record_15 in file solute.inp.

Imin-5. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

    LABEL: sub-header describing the data that follow.

Imin-6. Composition of the mineral zone

Variable: NAMIN VOL2 IKIN4M

Format: A, F, I   (free format, one record per mineral)

    NAMIN: name of the mineral present in the system, in quotes. The name of the mineral must be included among those previously listed in the definition of the system (Miner records), although the order may change, and it is not needed to repeat the complete list. However, names of minerals specified to react under equilibrium constraints all (and always) must precede the names of minerals reacting under kinetic constraints. Minerals defined for the system (Miner records) but excluded from the list are assumed to take zero values for all input parameters specified below. A trailing record (Imin-7) must end the list of minerals (for each given zone).

VOL2: initial volume fraction of the mineral, excluding liquid (mineral volume divided by total volume of solids). The sum of VOL2s need not add up to 1. If the sum is less than 1, the remaining solid volume fraction is considered nonreactive.

IKIN4M: flag for the mineral type:

IKIN4M = 0 for minerals at equilibrium.

IKIN4M = 1 for minerals under kinetic constraints. For minerals under kinetic constraints, an additional record (Imin-6.1, below) is always required.

IKIN4M = 2 to suppress reaction for either kinetic and/or equilibrium minerals.

Imin-6.1.

Variable: RAD, AMIN, IMFLG2

Format: 2F, I   (free format)

RAD: radius of mineral grain (in m) used to calculate surface area. RAD is used in conjunction with RNUCL (Miner-6) for precipitation of minerals not initially present, and in conjunction with current amounts for minerals initially present, as long as the calculated surface area from RAD is larger than the AMIN value specified below. Suggested values are RAD=1.0E-8 with RNUCL=1.0E-6. Using this option, surface areas will decrease as the mineral initially precipitates and grain size increases, down to the AMIN value specified below. If RAD = 0.0, this option is turned off, and surface areas are calculated using the AMIN value below.

AMIN: initial mineral reactive surface area. If a mineral is not initially present, and the option to use mineral grain size is turned off (RAD = 0.0), its surface area will be computed from the value of RNUCL specified on record Miner-6, as long the surface area computed in this way remains below AMIN. The units of AMIN depend on the value of flag IMFLG2 below.

IMFLG2: A flag to specify the units of input AMIN values (see Appendix G)

IMFLG2 = 0 for $cm^2_{mineral}/g_{mineral}$

IMFLG2 = 1 for $m^2_{mineral}/m^3_{mineral}$

IMFLG2 = 2 for $m^2_{rock}/m^3_{medium\ (total)}$

IMFLG2 = 3 for $m^2_{rock}/m^3_{medium\ (solids)}$

IMFLG2=3 and RAD=0.0 : the input surface area will remain constant

IMFLG2 = 4 (constant rate is input in mol/sec; surface area is not used)

Imin-7. Trailer for Imin records (one record after each zone)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.3.4   Initial and injection gas zones (Igas)

This section describes the initial and injection gas zones present in the system. These zones are mapped to the numerical grid through variables IZGSDF, IZBGDF,IZGS, and IZBG on Record_14 and Record_15, respectively, in file solute.inp. Note that H_2O gas is not entered in the list of gases here, because H_2O transport and thermodynamics are treated by the TOUGH2 EOS module selected for any given simulation. The injection gas zone IZBG is a new option for V3-OMP and must be added to files created for earlier TOUGHREACT versions.

Igas-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

   LABEL: comments or blank line.

Igas-2. Header for Igas records (a "Skip" record)

Variable: LABEL

Format: A (free format)

   LABEL: header describing Igas records.

Igas-3.

Variable: NGTYPE, NIGASZON

Format: 2I (free format)

   NGTYPE: total number of gas zones in the system.

   NIGASZON: total number of injection (boundary) gas zones in the system.

The following records Igas-4, Igas-5, Igas-6 and Igas-7 define each gas zone, and must be repeated NGTYPE times.

Igas-4.

Variable: IGTYPE

Format: I (free format)

   IGTYPE: Index of the gas zone. It must be 1 for the first zone, increasing sequentially thereafter.
      This index must correspond to one of the gas zone indices specified on Record_14 and
      Record_15 in file solute.inp. It is then set again to 1 for the first injection (boundary) gas,
      then increases again sequentially up to NBGTYPE.

Igas-5. Label

Variable: LABEL (a "Skip" record)

Format: A (free format)

LABEL: sub-heading describing the data that follow.

Igas-6. Composition of gas zone (partial pressure for initial gas, mole fraction for injected gas)

Variable: NAGAS   GASPP

Format: A, F (free format)

NAGAS: name of the gaseous species present in the system (in quotes). The name of the gas must be included among those previously listed in the definition of the system (Gas records), although the order may change, and it is not needed to repeat the complete list. Gases defined for the system (Gas records) but excluded from the list are assumed to take zero values for VOLG below. A trailing record (Igas-7) must end the list of gases (for each given zone).

GASPP: For initial gas zones, it is given as partial pressure of the gaseous species (in bars). If zero, grid blocks corresponding to this zone will be given a partial pressure equal to the fugacity of the gas at equilibrium with the aqueous solution in these blocks, as computed for initial and boundary waters (records Water) during initialization.

For injection (boundary) gas zones it is given as mole fraction of the injected gas composition. Note that the mole fraction should reflect the composition of the injected gas (e.g. CO_2, H_2O, etc.) defined in GENER.

Igas-7. Trailer for Igas records (one record after each zone)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.3.5   Zones for permeability-porosity relationships (Zppr)

This section describes zones where different correlations can be applied to compute the coupling of porosity with permeability. These zones are mapped to the numerical grid through variables IZPPDF and IZPP on Record_14 and Record_15, respectively, in file solute.inp.

Zppr-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments or blank line.

Zppr-2. Header for Zppr-2 records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Igas records

Zppr-3.

Variable: NPPZON

Format: I (free format)

NPPZON: Total number of permeability zones defined for the system.

The following records, Zppr-4, Zppr-5, and Zppr-6 define each permeability zone, and must be repeated NPPZON times. Note, in this case, the trailer record (Zppr-7) is required only once at the end of the list of all permeability zones.

Zppr-4.

Variable: IPPZON

Format: I (free format)

IPPZON: index of the permeability zone.   It must be 1 for the first zone, increasing sequentially thereafter. This index must correspond to one of the permeability-porosity zone indices specified on Record_14 and Record_15 in file solute.inp.

Zppr-5. Label

Variable: LABEL (a "Skip" record)

Format: A (free format)

LABEL: sub-heading describing the data that follow.

Zppr-6. Data related to zone for permeability-porosity relationship

Variable: ipptyp, aparpp, bparpp

Format: I, 2F   (free format)

Ipptyp: the index for the permeability law. Details on permeability-porosity relationships are described in Appendix F.

Ipptyp = 0: No change in permeability. Can be used to turn off permeability changes in specific zones.

Ipptyp = 1: Simplified Carman-Kozeny (Eq. F.7 in Appendix F). The parameter values (aparpp and bparpp) are not used and may be set to 0.0 or any real number.

Ipptyp = 2: Modified Hagen-Poiseulle Model. Permeability calculated from pore throat diameter, number of throats per pore, and number of pores per area using the Hagen-Poiseulle equation (modified from Ehrlich et al. 1991). Cubic packed spheres used to calculate pore throat diameters. The parameters are: (aparpp) number of effective throats per pore (typically about 2 to 3). (bparpp) number of pores per m^2 area.

Ipptyp = 3: Cubic law (Eq. F.2). The parameter values (aparpp and bparpp) are not used and may be set to 0.0 or any real number.

Ipptyp = 4: Modified cubic law (Eqs. F.3-F.6). The parameters are: (aparpp) *fracture porosity / fracture-matrix area* (analogous to fracture aperture) (m^3/m^2) and (bparpp) fracture spacing (*m*)

Ipptyp = 5: Verma-Pruess permeability-porosity relation (Eq. F.8). The parameters are: (aparpp) the value of "critical" porosity at which permeability goes to zero and (bparpp) a power law exponent. The initial porosity is taken as the value at *t* = 0, rather than the initial value which have changed for a restart simulation.

Ipptyp = 6: Matrix fractal pore space geometry (Pape et al., 1999). The parameters are: (aparpp) exponent on (ϕ/ϕ_0) for porosity ≤ 0.1, and (bparpp) exponent on (ϕ/ϕ_0) for porosity ≥ 0.1.

Zppr-7. Trailer for Zppr records (one record only, at end zone list)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.3.6   Surface adsorption zones (Zads)

This part is used to input zones with specific surface areas for surface complexation (adsorption). These zones are mapped to the numerical grid through variables IZADDF and IZAD on Record_14 and Record_15, respectively, in file solute.inp.

Zads-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments or blank line.

Zads-2. Header for Zads records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Zads records.

Zads-3.

Variable: NDTYPE

Format: I (free format)

NDTYPE: total number of surface adsorption zones defined for the system.

Zads-4. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: sub-heading describing the data that follow.

The following records, Zads-4, Zads-5, and Zads-6 define each adsorption zone, and must be repeated NDTYPE times. Note, in this case, the trailer record (Zads-6) is required only once at the end of the list of all adsorption zones.

Zads-5. Adsorption zone index and type

Variable: IDZONE   IEQUIL

Format: 2 I (free format)

IDZONE: index of the surface adsorption zone. It must be 1 for the first zone, increasing sequentially thereafter. This index must correspond to one of the adsorption zone indices specified on Record_14 and Record_15 in file solute.inp.

IEQUIL: flag for type of initialization.

=0 do not equilibrate the surface with initial aqueous solutions

=1 equilibrate the surface with initial aqueous solutions at each model grid block prior to starting flow/transport calculations. In such case, initial sorbed amounts are computed at each grid block, and for each surface, such that initial water compositions remain unchanged after sorption. Results of this initial surface equilibration can be output in file chdump.out if ichdump is set to 1 or 2 in solute.inp (on Record_2).

Zads-6. Adsorption surface area

Variable: NAME IFLAG S_AREA

Format: A, I, F (free format)

NAME: name of primary surface species, in quotes. The name must match one of the primary surface complex species entered at the end of the list of primary species at the top of the file (Prim records, species defined with NOTRANS=2).

IFLAG: flag to specify the units of the sorption surface area.

=0 $cm^2_{mineral}/g_{mineral}$. If NAADS_MIN = 'no_mineral' (on record Prim-2), internal conversions will assume a generic mineral density of 2.65 g/cm^3 for this surface.

=1 $m^2_{mineral}/m^3_{mineral}$

=2 $m^2_{mineral}/m^3_{medium\_solids}$

If NAADS_MIN starts with 'surface' (on record Prim-2), a constant surface area entered in units of m^2/kg$_{H2O}$ will be assumed.

S_AREA: surface area for sorption, in units as defined by the value of IFLAG and/or NAADS_MIN (on record Prim-2).

Zads-7. Trailer for Zads records (one record only, at end of zone list)

Variable: LABEL

Format: A (free format)LABEL: character string starting with '*' (including quotes) or blank record

6.3.7   Linear Kd zones (Zlkd)

This section describes the linear adsorption Kd zones initially present in the system. These zones are mapped to the numerical grid through variables IZKDDF and IZKD on Record_14 and Record_15, respectively, in file solute.inp.

Zlkd-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments or blank line.

Zlkd-2. Header for Zlkd records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Zads records

Zlkd-3.

Variable: KDTYPE

Format: I (free format)

KDTYPE: total number of Kd zones in the system.

The following records, Zlkd-4, Zlkd-5 and Zlkd-6, define each linear Kd zone, and must be repeated KDTYPE times.

Zlkd-4.

Variable: IDTYPE

Format: I (free format)

IDTYPE: index of the Kd zone. It must be 1 for the first zone, increasing sequentially thereafter. This index must correspond to one of the Kd zone indices specified on Record_14 and Record_15 in file solute.inp.

Zlkd-5. Label

Variable: LABEL (a "Skip" record)

Format: A (free format)

LABEL: sub-heading describing the data that follow.

Zlkd-6. Data related to the Kd zone

Variable: NAME, SDEN2, VKD2

Format: A, F, F (free format)

NAME : the name of primary aqueous species with Kd (in quotes), which can be listed in any order. The species spelling must be the same as defined previously.

SDEN2: the solid density (in kg/dm^3).

VKD2 is value of Kd (in kg^{-1} which is mass/kg solid divided by mass/l solution). If SDEN2=0.0, VKD2 automatically represents retardation factor (≥ 1).

Zlkd-7. Trailer for Zlkd records (one record only, at end of zone list)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.3.8   Cation exchange zones (Zexc)

This section describes the characteristics of the cation exchange capacity zones present in the system. These zones are mapped to the numerical grid through variables IZEXDF and IZEX on Record_14 and Record_15, respectively, in file solute.inp.

Zexc-1. Label (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: comments or blank line.

Zexc-2. Header for Zexc records (a "Skip" record)

Variable: LABEL

Format: A (free format)

LABEL: header describing Zexc records.

Zexc-3.

Variable: NXTYPE

Format: I (free format)

NXTYPE: total number of cation exchange zones.

Zexc-4. Label

Variable: LABEL

Format: A (free format)

LABEL: sub-heading describing the data that follow.

Zexc-5. Data related to the cation exchange zone
Zexc-5 must be repeated NXTYPE times. If NXTYPE is zero omit this card.

Variable: IXTYPE   NXsites(CEC)

Format: I,   NXsites(F)   (free format)

IXTYPE: index of the cation exchange zone. It must be 1 for the first zone, increasing sequentially thereafter. This index must correspond to one of the exchange zone indices specified on Record_14 and Record_15 in file solute.inp.

CEC: cation exchange capacity (meq/100 g of solid). Note also that there are NXsites values, exch for one exchange site

Zexc-7. Trailer for Zexc records (one record only, at end of zone list)

Variable: LABEL

Format: A (free format)

LABEL: character string starting with '*' (including quotes) or blank record

6.4   Thermodynamic Database

Aqueous species, minerals, and gases read in file chemical.inp must be found in the thermodynamic database file. The name of the database file is specified in file solute.inp. The format of the database file is free, and values for all input data (even if zero) must be supplied, unless specifically indicated otherwise. If any aqueous species, mineral, or gas is not in the supplied database or one desires to use different thermodynamic data, users must add these data to the database. An example of a chemical database file is given in Figure 6.4-1. The distribution files include a utility program for converting databases from other codes (such as EQ3/6 and PHREEQC) to the TOUGHREACT database format. The description of the conversion program is given in Appendix L. Appendix L also gives descriptions of other utility programs for switching basis (primary) species and regressing log(K) data.

TOUGHREACT V3.0-OMP has new options for reading in temperature-dependent coefficients for heat capacity, thermal conductivity, and thermal expansion of minerals as extra lines in the thermodynamic database. Although thermal expansion coefficients can be read in, the calculation of temperature-dependent mineral densities is not yet implemented. Another revision affects the use of the mineral molar volumes that are now read in as initial values that may change owing to swelling/shrinkage (and in a future version thermal expansion/contraction) during the simulation.

Spelling convention for reactants/products names

Names of all reactants and products must be input within quotes. On input, these strings are all converted to lower case characters. In addition, any multiple electronic charges incorporated into the names of cations and anions are converted to one charge sign followed by the number of charges. For example, 'CO3--' is converted to 'co3-2' and 'Al+++' is converted to 'al+3'. All names must be no more than 20 characters long. Longer names will be truncated. The use of a consistent spelling in the database is recommended, although the internal conversion to lower case characters and unique style for charge allow for input flexibility.

The following aqueous and gas species require specific spelling for proper internal handling of special functions with some EOS modules:

water	'H2O' or 'h2o'
hydrogen ion	'H+' or 'h+'
hydroxide anion	'OH-' or 'oh-'
carbon dioxide gas	'CO2(g)' or 'co2(g)'
hydrogen gas	'H2(g)' or 'h2(g)'
methane gas	'CH4(g)' or 'ch4(g)'
hydrogen sulfide gas	'H2S(g)' or 'h2s(g)'
sulfur dioxide gas	'SO2(g)' or 'so2(g)'
oxygen gas	'O2(g)' or 'o2(g)'
carbonic acid	'CO2(aq)' or 'co2(aq)'

bicarbonate	'HCO3-' or 'hco3-'
carbonate	'CO3-2' or 'co3-2'
methane (dissolved)	'CH4(aq)' or 'ch4(aq)'
hydrogen sulfide (dissolved)	'H2S(aq)' or 'h2s(aq)'
sulfur dioxide (dissolved)	'SO2(aq)' or 'so2(aq)'
oxygen (dissolved)	'O2(aq)' or 'o2(aq)'

End-of-header record (first record):

Variable: 'DUMMY'

Format: A

DUMMY: a label used to indicate the start of the database. This label must start with '!end-of-header', <u>without</u> quotes. All inputs prior to this record are skipped. All records after this record must follow the formatting and record order described below.

Temperature record:

Variable: 'DUMMY', NTEMP, (TEMPC(i), i=1,NTEMP)

Format: A, I, NTEMP(F)

DUMMY: a label (in quotes) used to describe the data for this record.

NTEMP : the number of TEMPC values to read.

TEMPC : temperatures (ºC) at which the log(K) data are listed in this file, at a given reference pressure P_0 (for databases distributed with TOUGHREACT, P_0=1 bar at T<100°C, and the saturation pressure of pure water at T≥100°C). TEMPC values must be listed in order of increasing temperature. These values are used to constrain log(K) extrapolation within this temperature range. Log(K)'s are not extrapolated outside this temperature range. For example, if the maximum TEMPC is 150ºC but the computed system temperature is 250ºC, log(K)'s will be extrapolated only to 150ºC (i.e. the geochemical speciation will be computed at 150ºC, not 250ºC). *Therefore, users must make sure that simulation temperatures are within the range of thermodynamic data temperatures.*

Basis (primary species) records:

Basis-1.

Variable: 'NAME', A0, Z, MWT

Format: A, 3F (one record per primary species)

NAME : name or chemical formula of aqueous basis species, in quotes (truncated after 20 characters).

A0 : Ion effective or hydrated radius used to compute the Debye-Hückel a0 parameter (see Appendix H for details). For neutral species other than typical dissolved gases (see Section H.3 of Appendix H), if A0 > 100, the value of A0 is used to compute a salting-out coefficient K_i

equal to A0 – 100 (i.e., salting-out coefficients for neutral species can be entered as values of A0 equal to 100+K_i; see Equation H.9 for the definition of K_i).

Z : the ion electric charge

MWT : Molecular weight of the aqueous species (g/mol).

This record is repeated as many times as the number of primary species.

Trailer record after Basis records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes.   This record indicates the end of the list of basis species, and must appear directly after the last basis species.

"Skip" records:

Starting from this point, any record beginning with either # (without quotes), or * followed by one blank (without quotes), or any blank record will be skipped on input. These "skip" records can be inserted anywhere in the database (after the first trailer record closing the list of basis species), as long as they are not inserted within records pertaining to the same reaction (i.e., these records can be inserted only <u>between</u> sets of records that pertain to one reaction). These "skip" records can be used for comments, data source references, or simply to clear the appearance of the database.

Secondary (derived) species records:

Data for individual secondary species are input as a set of 3 records, as follows:

Sec-1.

Variable: 'NAME', Xmwt, A0, Z, NCPS, (STQS(i), 'NAM(i)', i=1,NCPS)

Format: A, 3F, I, NCPS(F, A)

NAME : chemical formula of secondary species, in quotes (truncated after 20 characters).

Xmwt : molecular weight of the aqueous species (g/mol).

A0 : ion effective or hydrated radius (Angstrom) used to compute the Debye-Hückel a0 parameter (see Appendix H for details). For neutral species other than typical dissolved gases (see Section H.3 of Appendix H), if A0 > 100, the value of A0 is used to compute a salting-out coefficient K_i equal to A0 – 100 (i.e., salting-out coefficients for neutral species can be entered as values of A0 equal to 100+K_i; see Equation H.9 for the definition of K_i).

Z :   ion electric charge.

NCPS : number of basis species defining the secondary species.

STQS : stoichiometric coefficients of component (basis) species NAM included in the dissociation reaction of the derived species (negative and positive values for reactants and products, respectively). The derived species is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQS.

NAM : name of the reactant or product, in quotes (truncated after 20 characters; must match one of the basis species).

Sec-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of secondary species, as in Sec-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the given reaction at each discrete temperature listed in record Temp-1 above (at a reference pressure P^0). These data are generally skipped on input if log(K) regression coefficients as a function of temperature are entered on record Sec-3 (the discrete log(K) values should, however, always be included in the file to provide for easy reference to the data). If no regression coefficients are given on record Sec-3, AKLOG values are used to internally regress log(K) as a function of temperature on input. Note that AKLOG values equal to 500 are interpreted as "no data".

Sec-3.

Variable: 'NAME', (AKCOES(i), i=1,5), (AKCOP(i), i=1,5)

Format: A, 5(E), 5(E)

NAME : name or chemical formula of secondary species, as in Sec-1.

AKCOES : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature (at a reference pressure P^0) with $\log_{10}(K)_{T,P0} = a*\ln(T_k) + b + c*T_k + d/T_k + e/T_k^2$, where T_k is absolute temperature (K), and *ln* stands for natural logarithm. Values must be entered for all coefficients. If all coefficient values are omitted, the coefficients will be internally computed from AKLOG values input on record Sec-2.

AKCOP : (optional) contains regression coefficients a, b, c, d, and e to calculate the volume change ΔV (in cm^3/mol) for the reaction as a function of temperature (average ΔV over the pressure interval P^0 to P), with $\Delta V = a + b*T_k + c*T_k^2 + d/T_k + e/T_k^2$. This option is enabled with $a \neq 0$, in which case all coefficients must be entered. These coefficients are used to correct log(K) values as a function of pressure, with $\log_{10}(K)_{T,P} = \log_{10}(K)_{T,P0} - \Delta V*(P-P^0)/(2.303RT_k)$, where R is the gas constant.

Records Sec-1, Sec-2, and Sec-3 are repeated as sets of triplets, as many times as the number of secondary species. Each set can be spaced by as many "skip" records as desired.

Trailer record after secondary species records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of secondary species, and must appear anywhere between the last secondary species and first mineral.

Mineral Records:

The data for each mineral are input as a set of 3 records, as follows:

Mineral-1.

Variable: 'NAME', MOLWT, VMIN0, NCPM, (STQM(i), 'NAM(i)', i=1,NCPM)

Format: A, 2F, I, NCPM(F, A)

NAME : name or chemical formula of a mineral, in quotes (truncated after 20 characters).

MOLWT : molecular weight (g/mol).

VMIN0: initial molar volume of mineral, which can change during the simulation owing to swelling/shrinkage if invoked (cm^3/mole). If negative, a fourth line for temperature-dependent heat capacity coefficients will be read, and the VMIN0 will be reset to a positive value.

NCPM : the number of component species defining the mineral.

STQM : contains the stoichiometric coefficient of basis species NAM in the dissociation (hydrolysis) reaction of the mineral (negative and positive values for reactants and products, respectively). The mineral species is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQM.

NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the basis species).

Mineral-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of the mineral, as in Mineral-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the reaction at various temperatures. See record Sec-2 for formatting and other details.

Mineral-3.

Variable: 'NAME', (AKCOEM(i), i=1,5), (AKCOP(i), i=1,5)

Format: A, 5(E)

NAME : name or chemical formula of the mineral, as in Mineral-1.

AKCOEM : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature. See record Sec-3 for formatting and details.

AKCOP : (optional) contains regression coefficients a, b, c, d, and e to calculate ΔV for the reaction (in cm^3/mol) as a function of temperature. See record Sec-3 for formatting and details.

Mineral-4. Optional Record, if molar volume (VMIN0) is input as a negative value

Variable: 'NAME', NITL, (CPMNCF(i), i=1,4)

Format: A, I, 4(E)

NAME : name or chemical formula of the mineral, as in Mineral-1.

NITL : number of additional lines with thermal parameters including this one

CPMNCF : Coefficients for temperature-dependent heat capacity

Mineral-5. Optional Record, if molar volume (VMIN0) is input as a negative value and NITL ≥2

Variable: 'NAME', (TCMNCF(i), i=1,2)

Format: A, 2(E)

NAME : name or chemical formula of the mineral, as in Mineral-1.

TCMNCF: Coefficients for temperature-dependent thermal conductivity

Mineral-5. Optional Record, if molar volume (VMIN0) is input as a negative value and NITL =3

Variable: 'NAME', (ALPHTM(i), i=1,3)

Format: A, 3(E)

NAME : name or chemical formula of the mineral, as in Mineral-1.

ALPHTM: Coefficients for temperature-dependent thermal expansion

Trailer record after Mineral records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes.   This record indicates the end of the list of minerals, and must appear anywhere between the last mineral and first gas.

Gas records:

The data for each gas species are input as a set of 3 records, as follows:

Gas-1.

Variable: 'NAME', DMOLWT, DMDIAM, NCPG, (STQG(i), 'NAM(i)', i=1,NCPG)

Format: A, 2F, I, NCPG(F, A)

NAME : name or chemical formula of a gas species, in quotes (truncated after 20 characters).

DMOLWT : molecular weight (g/mol)

DMDIAM: molecular diameter (m) used to calculate gas diffusion coefficient (see Eq. (A.1) in Appendix A)

NCPG : the number of basis species defining the gas.

STQG : contains the stoichiometric coefficient of component species NAM in the dissociation reaction of the gas (negative and positive values for reactants and products, respectively). The gas is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQG.

NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the basis species).

Gas-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

NAME : name or chemical formula of the gas, as in Gas-1.

AKLOG : contains the equilibrium constants (log(K) in base 10) for the reaction at various temperatures. See record Sec-2 for formatting and other details.

Gas-3.

Variable: 'NAME', (AKCOEG(i), i=1,5), (AKCOPG(i), i=1,5)

Format: A, 5(E)

NAME : name or chemical formula of the gas, as in Gas-1.

AKCOEG : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature. See record Sec-3 for formatting and details.

AKCOPG : (optional) contains regression coefficients a, b, c, d, and e to calculate ΔV for the reaction (in cm^3/mol) as a function of temperature. See record Sec-3 for formatting and details.

Records Gas-1, Gas-2, and Gas-3 are repeated as sets of triplets, as many times as the number of secondary species. Each set can be spaced by as many "skip" records as desired.

Trailer record after Gas records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes. This record indicates the end of the list of gases, and must appear anywhere between the last gas and first surface complex.

Surface complex records:

The data for each surface complex are input as a set of 3 records, as follows:

Surface-1.

Variable: 'NAME', Z, NCPS, (STQS(i), 'NAM(i)', i=1,NCPS)

Format: A, F, I, NCPS(F, A)

  NAME : chemical formula of surface complex, in quotes (truncated after 20 characters).

  Z : electric charge of surface complex.

  NCPS : number of basis species defining the surface complex.

  STQS: stoichiometric coefficients of component species NAM included in the dissociation reaction of the surface complex (negative and positive values for reactants and products, respectively). The surface complex is always assumed to have a stoichiometric coefficient of -1.0, which is not included in STQS.

  NAM: name of the reactant or product, in quotes (truncated after 20 characters; must match one of the basis species).

Surface-2.

Variable: 'NAME', (AKLOG(i), i=1,ntemp)

Format: A, ntemp(F)

  NAME : name or chemical formula of the surface complex, as in Surface-1.

  AKLOG : contains the equilibrium constants (log(K) in base 10) for the reaction at various temperatures. See record Sec-2 for formatting and other details.

Surface-3.

Variable: 'NAME', (AKCOE(i), i=1,5)

Format: A, 5(E)

  NAME : name or chemical formula of the surface complex, as in Surface-1.

  AKCOE : contains regression coefficients a, b, c, d, and e to calculate $\log_{10}(K)$ as a function of temperature. See record Sec-3 for formatting and details.

Records Surface-1, Surface-2, and Surface-3 are repeated as sets of triplets, as many times as the number of surface complexes. Each set can be spaced by as many "skip" records as desired.

Trailer record after Surface records:

Variable: 'DUMMY'

Format: A

DUMMY: must spell 'end' or 'null', including quotes.   This record indicates the end of the list of secondary species, and must appear anywhere after the last surface complex.

```
      Any text here, for any number of records

      !end-of-header      Do not remove this record!
      'Temperature points:' 8 0.01 25.0 60.0 100.0 150.0 200.0 250.0 300.0
      'H2O'                         0.00  0.00    18.015
      'Ca++'                        2.87  2.00    40.078
      'Cl-'                         1.81 -1.00    35.453
      'Fe++'                        2.62  2.00    55.845
      'H+'                          3.08  1.00     1.008
      'HCO3-'                       2.10 -1.00    61.017
      'K+'                          2.27  1.00    39.098
      'Na+'                         1.91  1.00    22.990
      'Hfo_sOH'                     0.00  0.00     0.000
      'null'

      ####################
      # Aqueous species #
      ####################
      'CO2(aq)'      44.010  0.00  0.00    3  -1.00000 'H2O'  1.00000 'H+'  1.00000 'HCO3-'
      'CO2(aq)' -6.5804   -6.3447   -6.2684   -6.3882   -6.7235   -7.1969   -7.7868   -8.5280
      'CO2(aq)' 0.10476478E+03 -0.67138541E+03 -0.10862163E+00 0.38868294E+05 -0.26528340E+07
      # Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

      'NaSO4-'      119.053  1.81 -1.00    2   1.00000 'Na+'  1.00000 'SO4--'
      'NaSO4-'  -0.6765   -0.7000   -0.8416   -1.0629   -1.3893   -1.7724   -2.2416   -2.8730
      'NaSO4-' 0.15443167E+03 -0.98620007E+03 -0.14872193E+00 0.56350439E+05 -0.34707590E+07
      # Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

      'null'

      ####################
      #    Minerals      #
      ####################

      'Calcite'  100.087    36.934    3  -1.00000 'H+'  1.00000 'Ca++'  1.00000 'HCO3-'
      'Calcite' 2.2257    1.8487    1.3330    0.7743    0.0999   -0.5838   -1.3262   -2.2154
      'Calcite' 0.14237876E+03 -0.90313945E+03 -0.14436024E+00 0.50619704E+05 -0.29300495E+07
      # Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

      'Carnallite' 277.853 172.580 4 1.00000 'K+' 1.00000 'Mg++' 3.00000 'Cl-'  6.00000 'H2O'
      'Carnallite' 500.0000 4.2721 500.0000  500.0000  500.0000  500.0000  500.0000  500.0000
      'Carnallite' 0.00000000E+00 0.42721000E+01 0.00000000E+00 0.00000000E+00 0.00000000E+00
      # Data source:     EQ3/6 database data0.ymp.R5 YM Project SN0612T0502404.14

      'albit-hi'  262.220  -101.087    5   1.0000 'Na+'  1.0000 'Al+3'  3.0000 'SiO2(aq)'  2.0000
      'H2O'  -4.0000 'H+'
      'albit-hi'  500.0000    2.4190    1.2295   -0.0790   -1.4780   -2.6340   -3.6460   -4.6260
      'albit-hi'  0.12199909E+03 -0.81331114E+03 -0.96626546E-01 0.58330172E+05 -0.41063786E+07
      'albit-hi'  3   452. -.13364e-1 -1275900. -3953.6
      'albit-hi'      0.0 0.0
      'albit-hi'      2.762 -1.6329e-5 0.0
      # source:     HP98; Cp(T) from Holland and Powell JMG 2011
```

```
'null'
####################
#    Gases         #
####################

'CO2(g)' 44.010 2.5e-10 3 -1.00000 'H2O' 1.00000 'H+' 1.00000 'HCO3-'
'CO2(g)'  -7.7695 -7.8257 -8.0437 -8.3390 -8.7356 -9.2136 -9.7552 -10.3962
'CO2(g)' 9.833583157 -59.02305875 -0.026997768 950.3210943 0.0 -30.76062599 0.126305497 -
5.45461E-05 9039.990466 0.0
# Data source:     Regressed from Spycher and Pruess (2009)
# The coefficients for P correction correspond to dV=-32.6 cm3 up to 100C, then
#   increase to -39.4 at 300C
# Note, these values are for the CO2(g)=>CO2(aq) reaction, so dV must be zero
#   for CO2(aq)=>HCO3- reaction
'null'



########################
#    Surface complexes  #
########################

'Hfo_sOH2+' 1.000   2  1.00000 'Hfo_sOH'  1.00000 'H+'
'Hfo_sOH2+'500.0000 -7.2900 500.0000  500.0000  500.0000  500.0000  500.0000  500.0000
'Hfo_sOH2+' 0.00000000E+00 -0.72900000E+01 0.00000000E+00 0.00000000E+00 0.00000000E+00
# source:  (phreeqc) minteq.v4.dat 85 2005-02-02

'null'
```

7   Anticipated Error Messages

All execution stops built into TOUGHREACT are accompanied by a message indicating why the execution was aborted. These messages are written to file runlog.out. Some error messages do not lead to a program interruption. However, nonconvergence or division-by-zero in some routines may lead to the program crashing with little or no message. In these cases it is useful to check the files for detailed messages and/or examine the files to see which part of the code may have had troubles (e.g., flow, transport, or reaction). It may be necessary to rerun the simulation writing output (e.g., iter.out, chdump.out) more frequently. Only messages related to the reactive transport part of the program are reviewed below. Error messages originating from fluid and heat flow calculations are the same as for TOUGH2 V2 (Pruess et al., 1999).

7.1   From Routine: INIT (reads the CHEMICAL.INP file)

Most of these messages are self-explanatory and refer to exceeded array dimensions or other errors encountered when reading the chemical.inp file. Array dimension problems can be corrected by reducing the problem size or changing array dimensions in the source file chempar23.inc and recompiling the program. Some examples are given as follows:

Error: maximum number of component species (MPRI) was exceeded. Current max=(MPRI)
Execution stop: yes. Self-explanatory.

Error: maximum number of minerals (MMIN) was exceeded. Current max= (MMIN)
Execution stop: yes. Self-explanatory.

error reading aqueous species of the system
Execution stop: yes. Self-explanatory.

error reading minerals of the system
Execution stop: yes. Self-explanatory.

error reading gases of the system
Execution stop: yes. Self-explanatory.

error reading initial water zone= ___ (iwtype)
Execution stop: yes. Self-explanatory.

error reading initial mineral zone= ___ (imtype)
Execution stop: yes. Self-explanatory.

error reading initial gas zone= ___ (imtype)
Execution stop: yes. Self-explanatory.

7.2   From Routine: NRINIT (initial Newton-Raphson iterations)

ERROR (convergence problem in initialization of water composition)
Please adjust convergence criteria regarding chemical iteration
and initial guess of concentration of primary species
Execution stop: yes. Self-explanatory. This error results in calling routine chdump for troubleshooting (i.e. the last chemical speciation data are output in the chdump.out file). This error occurs during the initial geochemical speciation of waters specified in chemical.inp (no minerals, before the first time step). Check the *chdump.out* file for clues, and also check that water temperatures specified in chemical.inp data are not too different than the initial condition of temperature specified in the flow.inp file.

7.3   From Routine: READTHERM (reads thermodynamic database file)

All these messages occur while reading the thermodynamic database and are self-explanatory. These indicate improperly formatted records in the database file. All errors result in a program execution stop. Some examples are:

Error reading temperature data: stop
Error reading primary species: stop
Error reading secondary species: stop (followed by the species name)
Error reading minerals: stop (followed by the mineral name)
Error reading gases: stop (followed by the gas name)
Error reading adsorbed species: stop (followed by the species name)
Error in opening database file: stop

7.4   From Routine: READSOLU (reads the file solute.inp)

There are currently no specific error messages generated while reading the file solute.inp. The unit number of this file is 31. System error messages relating to this I/O number originate while reading this file. Make sure the fixed formats of this file are respected.

7.5   From Routine: CR_CP (kinetic data calculations)

error in data option for mineral (kinetic)= ___
Execution stop: yes. This message occurs if the flag IDEP for any of the kinetic minerals is not set to either 0 or 1. With this program version, IDEP must always be zero (this flag is specified in the mineral section of the chemical.inp file).

7.6   From Routine: NEWTONEQ (Newton-Raphson iterations after 1st time step)

ERROR: chemistry did not converge at node ___ (routine NEWTONEQ)

Species: ___   Error=___   Error limit= ___ relative

Node temperature (C): ___

Program execution was not aborted. Check results!
Execution stop: only if this error occurs at more than fifty grid blocks at any given time step. This error also calls routine chdump for troubleshooting (i.e., the last chemistry calculation data are output in the *chdump.out* file). This error occurs during the block-by-block geochemical speciation computations after the first time step (complete system, with minerals and gases if any). Check the *chdump.out* file for clues on why convergence was not reached. You may need to increase the loop limit (MAXITCH) and/or tolerance (TOLCH) in the solute.inp file. If boiling occurs, you may try increasing ST1MIN or decreasing STIMAX (specified in *solute.inp*). Chemical convergence may also fail because of errors during transport, resulting in erroneous system compositions that cannot yield a solution to geochemical speciation calculations. In this case, the time step may be decreased and/or the Courant number option enabled (RCOUR in *solute.inp* input file). Depending on the type of problem, chemical speciation in closely spaced grid blocks can be skipped by setting D1MAX > 0 (last resort).

Error: Negative concentration for species ___
Execution stop: no. Self-explanatory. A concentration may temporarily become negative during the chemical Newton-Raphson iterations, but should not remain negative. This error may indicate problems to come. It is rarely encountered.

8   Concluding Remarks

TOUGHREACT V3-OMP is a comprehensive computer program for non-isothermal multiphase fluid flow and geochemical transport. The code is applicable to porous media as well as to fractured rocks. An integral finite difference (IFD) technique is employed for space discretization. The IFD methodology can deal with irregular grids, does not require reference to a global system of coordinates, and includes classical dual-continua, multiple interacting continua, and multi-region models for heterogeneous and fractured rocks. Non-isothermal effects are considered, including water-vapor phase change and air partitioning between the

liquid and gas phases, temperature-dependence of thermophysical properties such as phase density and viscosity, and chemical properties such as thermodynamic and kinetic parameters. Chemical reactions considered under the local equilibrium assumption include aqueous complexation, acid-base, redox, gas dissolution/exsolution, cation exchange, and surface complexation. Mineral dissolution/precipitation can proceed either subject to local equilibrium or kinetic conditions. The gas phase is considered active for multiphase fluid flow, species transport, and gas-liquid chemical reactions.

TOUGHREACT V3-OMP is applicable to one-, two-, or three-dimensional geologic domains with physical and chemical heterogeneity, and can be applied to a wide range of subsurface conditions. Temperatures for multiphase flow can reach a maximum of the supercritical point of water at water saturation pressure ($\sim$374 °C) although the temperature range for equilibrium constants is generally from 0 to 300 °C, limited at present by available geochemical databases such as EQ3/6 (Wolery, 1992). Pressures of 1 bar (atmospheric pressure) to several hundred bars (at several thousand meter depth) can be considered. Water saturation can range from completely dry to fully water saturated. The code can handle ionic strengths from dilute to saline waters with up to 6 mol/kg for an NaCl-dominant solution.

TOUGHREACT applications have been demonstrated for a variety of reactive fluid and geochemical transport systems, including (1) contaminant transport with linear Kd adsorption and decay, (2) natural groundwater quality evolution under ambient conditions, (3) assessment of nuclear waste disposal sites, (4) sedimentary diagenesis and CO_2 geological sequestration in deep saline formations, (5) mineral deposition such as supergene copper enrichment, (6) mineral alteration and silica scaling in hydrothermal systems under natural and production conditions, and (7) acidic mine drainage and groundwater contamination. Of course, many other potential geologic, experimental, and engineered systems could be analyzed using similar methodologies as given in these examples.

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Appendix A Mathematical Equations for Flow and Transport

All flow and transport equations have the same structure, and can be derived from the principle of mass (or energy) conservation. Table A-1 summarizes these equations and Table A-2 gives the meaning of symbols used. The models for fluid and heat flow are discussed in detail by Pruess (1987 and 1991) and Pruess et al. (1999). Aqueous species are subject to transport in the liquid phase and local chemical interaction with the solid and gaseous phases. Chemical transport equations are written in terms of total dissolved concentrations of chemical components comprised of concentrations of their basis species plus their associated aqueous secondary species (Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Walter et al., 1994). Advection and diffusion are considered for chemical transport, and diffusion coefficients are assumed to be the same for all aqueous species.

Table A—1   **Governing equations for fluid and heat flow, and chemical transport. Symbol meanings are given in Table A-2. Take EOS3 and EOS4 flow modules as example. For EOS2 and ECO2N, component 'Air' in the table should be replaced with 'CO$_2$'. For EOS1, equation for air is not required. For EOS9, equations for air and heat are not required (only Richard's equation).**

General governing equations:
$$\frac{\partial M_\kappa}{\partial t} = -\nabla F_\kappa + q_\kappa$$

Water: $M_w = \phi(S_l\rho_l X_{wl} + S_g\rho_g X_{wg})$ $F_w = X_{wl}\rho_l\mathbf{u}_l + X_{wg}\rho_g\mathbf{u}_g$ $q_w = q_{wl} + q_{wg}$

Air: $M_c = \phi(S_l\rho_l X_{cl} + S_g\rho_g X_{cg})$ $F_c = X_{cl}\rho_l\mathbf{u}_l + X_{cg}\rho_g\mathbf{u}_g$ $q_c = q_{cl} + q_{cg} + q_{cr}$

Heat: $M_h = \phi(S_l\rho_l U_l + S_g\rho_g U_g) + (1-\phi)\rho_s U_s$ $F_h = \sum_{\beta=l,g} h_\beta\rho_\beta\mathbf{u}_\beta - \lambda\nabla T$ q_h

$$\text{where } \mathbf{u}_\beta = -k\frac{k_{r\beta}}{\mu_\beta}\left(\nabla P_\beta - \rho_\beta\mathbf{g}\right) \quad \beta = l, g \qquad \text{(Darcy's Law)}$$

Chemical components in the liquid phase ($j = 1, 2, \ldots, N_l$):

$$M_j = \phi S_l C_{jl} \qquad\qquad F_j = \mathbf{u}_l C_{jl} - (\tau\phi S_l D_l)\nabla C_{jl} \qquad\qquad q_j = q_{jl} + q_{js} + q_{jg}$$

$\tau_\beta = \phi^{1/3} S_\beta^{7/3}$ (Millington and Quirk, 1961)

Table A—2 **Symbols used in Table A-1.**

	component concentration, mol L^{-1}		density, kg m^{-3}
	diffusion coefficient, m^{2}s^{-1}		viscosity, kg m^{-1}s^{-1}
	mass flux, kg m^{-2}s^{-1} (*)		heat conductivity, W m^{-1}K^{-1}
	permeability, m^2		
$_r$	relative permeability	Subscripts:	
	gravitational acceleration, m s^{-2}	air	
	mass accumulation, kg m^{-3}	gas phase	
	number of chemical components	heat	
	pressure, Pa	aqueous chemical component	
	source/sink	liquid phase	
	saturation	reaction	
	temperature, ^{o}C	solid phase	
	internal energy, J kg^{-1}	water	
	Darcy velocity, m s^{-1}	governing equation index	
	mass fraction	phase index	
	porosity	medium tortuosity	

(*) For chemical transport and reaction calculations, molar units are used instead of kg.

The primary governing equations given in Table A-1 must be complemented with constitutive relationships that express all parameters as functions of thermophysical and chemical variables. The expressions for non-isothermal multiphase flow are given by Pruess et al. (1999). The expressions for chemical reactions are given in Appendix B.

Gas species diffusion coefficients are computed as a function of temperature, pressure, molecular weight, and molecular diameter. Assuming ideal gas behavior, the tracer diffusion coefficient of a gaseous species can be expressed as follows (Lasaga, 1998):

$$D = \frac{RT}{3\sqrt{2}\pi P N_A d_m^2} \sqrt{\frac{8RT}{\pi M}}$$

(A. 1)

where:

D = diffusion coefficient (m^2/s)
R = molar gas constant (8.31451 m^{2}kg s^{-2}mol^{-1} K^{-1})
T = temperature in Kelvin units
π = 3.1415926536
P = pressure (kg m^{-1} s^{-2})
N_A = Avogadro's number (6.0221367 × 10^{23} molecules/mol)
D_m = molecular diameter (m)
M = molecular weight (kg/mol)

Appendix B Mathematical Formulation of Chemical Reactions

To represent a geochemical system, it is convenient to select a subset of N_C aqueous species as basis species (or component or primary species). All other species are called secondary species that include aqueous complexes, precipitated (mineral) and gaseous species (Reed, 1982; Yeh and Tripathi, 1991; Steefel and Lasaga, 1994). The number of secondary species must be equal to the number of independent reactions. Any of the secondary species can be represented as a linear combination of the set of basis species such as

$$S_i = \sum_{j=1}^{N_C} v_{ij} S_j \qquad i = 1,..., N_R$$

(B.1)

where S represents chemical species, j is the basis species index, i is the secondary species index, N_R is the number of reactions (or secondary species), and v_{ij} is the stoichiometric coefficient of j-th basis species in the i-th reaction.

B.1 Kinetic reactions among primary species

These type of reactions include aqueous and sorption reaction kinetics and biodegradation. A general-rate law is used,

$$r_i = \sum_{s=1}^{M} \begin{bmatrix} k_{i,s} & \text{rate constant} \\ \times \prod_{j=1}^{N_l} \left(\gamma_j^{v_{i,j}} C_j^{v_{i,j}} \right) & \text{product terms} \\ \times \prod_{k=1}^{N_m} \dfrac{C_{i,k}}{K_{Mi,k} + C_{i,k}} & \text{Monod terms} \\ \times \prod_{p=1}^{N_p} \dfrac{I_{i,p}}{I_{i,p} + C_{i,p}} & \text{inhibition terms} \end{bmatrix}$$

(B.2)

where r_i is the reaction rate of the i-th reaction, M is the number of mechanisms or pathways and s is the mechanism counter, k is a rate constant, (often denoted v_{max}, maximum specific growth constant for biodegradation), γ_j is the activity coefficient of species j, C_j is the concentration of species j (with biodegradation the product term is usually biomass concentration), $v_{i,j}$ is a stoichiometric coefficient, N_l is the number of reacting species in the forward rate term (called product terms), N_m is the number of Monod factors (Monod terms), $C_{i,k}$ is the concentration of the k-th Monod species, $C_{i,p}$ is the concentration of the p-th inhibiting species, $K_{Mi,k}$ is the k-th Monod half-saturation constant of the i-th species, N_P is the number of inhibition factors (inhibition terms), and $I_{i,p}$ is the p-th inhibition constant. Equation (B.2) accounts for multiple mechanisms and multiple products, Monod, and inhibition terms, which can cover many rate expressions (examples of rate expression are given in Samples 9 and 10).

B.2   Aqueous complexation

These reactions are assumed to be at local equilibrium. By making use of the mass action equation to the dissociation of the i-th aqueous complex (Equation B.1), concentrations of aqueous complexes can be expressed as functions of the concentrations of basis species:

$$c_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_c} c_j^{\nu_{ij}} \gamma_j^{\nu_{ij}} \qquad\qquad \text{(B.3)}$$

where c_i is molal concentration of the i-th aqueous complex, and c_j is molal concentration of the j-th basis species, γ_i and γ_j are thermodynamic activity coefficients (details on calculation of activity coefficients are given in Appendix H), and K_i is the equilibrium constant.

B.3   Equilibrium mineral dissolution/precipitation

The mineral saturation ratio can be expressed as

$$\Omega_m = K_m^{-1} \prod_{j=1}^{N_C} c_j^{\nu_{mj}} \gamma_j^{\nu_{mj}} \qquad\qquad m = 1...N_P \qquad\qquad \text{(B.4)}$$

where m is the equilibrium mineral index, and K_m is the corresponding equilibrium constant. At equilibrium, we have

$$SI_m = \log_{10} \Omega_m = 0 \qquad\qquad \text{(B.5)}$$

where SI_m is called the mineral saturation index. The treatment for mineral solid solutions is given in Appendix I.

B.4   Kinetic mineral dissolution/precipitation

Kinetic rates could be functions of non-basis species as well. Usually the species appearing in rate laws happen to be basis species. In this model, we use a rate expression given by Lasaga et al. (1994):

$$r_n = f(c_1, c_2,..., c_{N_C}) = \pm k_n A_n \left| 1 - \Omega_n^{\theta} \right|^{\eta} \qquad\qquad n = 1...N_q \qquad\qquad \text{(B.6)}$$

where positive values of r_n indicate dissolution, and negative values precipitation, k_n is the rate constant (moles per unit mineral surface area and unit time) which is temperature dependent, A_n is the specific reactive surface area per kg H_2O (details on A_n calculations are given in Appendix G), Ω_n is the kinetic mineral saturation ratio defined in (B.4). The parameters θ and η must be determined from experiments; usually, but

not always, they are taken equal to one. The temperature dependence of the reaction rate constant can be expressed reasonably well via an Arrhenius equation (Lasaga, 1984; Steefel and Lasaga, 1994). Because many rate constants are reported at 25°C, it is convenient to approximate rate constant dependency as a function of temperature, thus

$$k = k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \tag{B.7}$$

where Ea is the activation energy, k25 is the rate constant at 25°C, R is gas constant, T is absolute temperature.

Carroll et al. (1998) noted that the rates of amorphous silica precipitation based on Rimstidt and Barnes (1980) are about three orders of magnitude lower than those observed in geothermal systems. Carroll et al. (1998) presented experimental data on amorphous silica precipitation for more complex geothermal fluids at higher degrees of supersaturation, and also for a near-saturation simple fluid chemistry. Under conditions far from equilibrium, the rate law for amorphous silica precipitation has been expressed as:

$$r = kA(\Omega)^\theta \tag{B. 8}$$

This rate does not tend to zero as Ω goes to one, and therefore, in TOUGHREACT, a modification was made to this law so that it tends to zero as Ω approaches one

$$r = kA\left[(\Omega)^\theta - \frac{1}{\Omega^{2\theta}}\right] \tag{B. 9}$$

The pH dependence of mineral precipitation and dissolution rates is calculated using the following expressions:

$$k_{adj} = k\ (10^{-pHc}/10^{-pH1})^{slope1} \qquad \text{if pHc < pH1} \tag{B.10}$$

$$k_{adj} = k\ (10^{-pHc}/10^{-pH2})^{-slope2} \qquad \text{if pHc > pH2} \tag{B.11}$$

where k_{adj} is the rate adjusted for pH, k is the original rate (Equation B.6), pH_c is the current (calculated) pH, $pH1$ is the pH below which the rate is adjusted by $slope1$ and $pH2$ is the pH above which the rate is adjusted by $slope2$. Parameters $slope1$ and $slope2$ are the absolute values (both positive numbers) of the log(k) versus pH slopes below $pH1$ and above $pH2$, respectively (Figure B.4-1). Between these two pH values, the rate is assumed to remain independent of pH.

Figure B.4—1 Variation of reaction rate with pH. Slopes shown are for the dissolution of silicate and aluminosilicate minerals (After Drever, 1997).
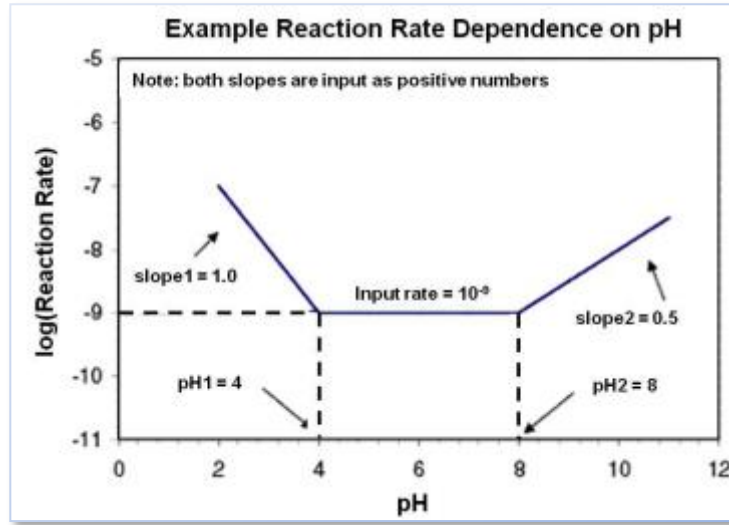
The kinetic rate constant (k) in Eqs. (B.6) and (B.7) only considers the most well-studied mechanism in pure H_2O (at neutral pH). Dissolution and precipitation of minerals are often catalyzed by H^+ (acid mechanism) and OH^- (base mechanism). For many minerals, the kinetic rate constant k includes each of these three mechanisms (Lasaga et al., 1994; Palandri and Kharaka, 2004), or

$$k = k_{25}^{nu} \exp\left[\frac{-E_a^{nu}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + k_{25}^{H} \exp\left[\frac{-E_a^{H}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_H^{n_H}$$
$$+ k_{25}^{OH} \exp\left[\frac{-E_a^{OH}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_{OH}^{n_{OH}}$$

(B.12)

where superscripts or subscripts nu, H, and OH indicate neutral, acid and base mechanisms, respectively; a is the activity of the species; and n is power term (constant). Notice that parameters θ and η (see Eq. B.6) are assumed the same for each mechanism. The rate constant k can be also dependent on other species such as Al^{3+} and Fe^{3+}. Two or more species may be involved in one mechanism. A general form of species dependent rate constants (extension of Eq. B.12) is coded in TOUGHREACT, or,

$$k = k_{25}^{nu} \exp\left[\frac{-E_a^{nu}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + \sum_i k_{25}^{i} \exp\left[\frac{-E_a^{i}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \prod_j a_{ij}^{n_{ij}}$$

(B.13)

where superscripts or subscripts i is the additional mechanism index, and j is species index involved in one mechanism that can be primary or secondary species. TOUGHREACT considers up to five additional

mechanisms and up to five species involved in each mechanism. An application of multiple mechanisms (Eq. B.13) can be found in the CO_2 disposal sample problem (Section 8.5).

The precipitation of a mineral can be suppressed up to a given, positive saturation index value, $\log(\Omega)_w$. Within this "supersaturation window", the mineral is not allowed to precipitate. The mineral precipitates if its saturation index $\log(\Omega) \geq \log(\Omega)_w$, and dissolves if $\log(\Omega) < 0$. The size of the window can be set to decrease exponentially with temperature as follows:

$$(\Omega)_{w,T} = \log(\Omega)_{w,T0} \exp(-4.61(T- T_0)/(T_1-T_0)) \tag{B.14}$$

where $\log(\Omega)_{w,T}$ is the window at the current temperature T and $\log(\Omega)_{w,T0}$ is the initial (input) window at temperature T_0. T_1 is the temperature at which the window is one-hundredth the size of the initial window (thus the temperature at which the effect of the window essentially disappears, see Figure B.4-2). Values of $\log(\Omega)_{w,T0}$, T_0, and T_1 are provided as input parameters.

Figure B.4—2   Supersaturation window dependence on temperature.
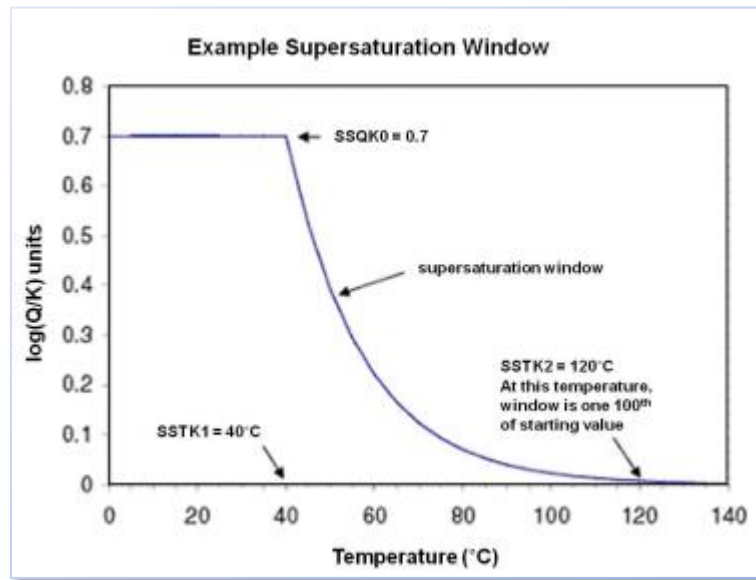
B.5   Gas dissolution/exsolution

Reactions involving aqueous and gaseous phases are usually assumed to be at equilibrium. According to the Mass-Action Law, one has:

$$P_f \Gamma_f K_f = \prod_{i=1}^{N_c} c_i^{\nu_{fi}} \gamma_i^{\nu_{fi}} \tag{B.15}$$

where subscript f is gas index, p is the partial pressure (in bar), Γ is the gas fugacity coefficient. For low pressures (in the range of atmospheric pressure), the gaseous phase is assumed to behave like an ideal mixture, and the fugacity coefficient Γ is assumed equal to one. At higher temperatures and pressures, such as boiling conditions in hydrothermal systems and CO_2 disposal in deep aquifers, the assumption of ideal gas and ideal mixing behavior is not valid, and the fugacity coefficients should be corrected according to temperatures and pressures (Spycher and Reed, 1988). For example, for H_2O-CO_2 mixtures in boiling conditions, we assume that H_2O and CO_2 are real gases, but their mixing is ideal. Following Spycher and Reed (1988), the fugacity coefficients is calculated from

$$\ln \Gamma = \left(\frac{a}{T^2} + \frac{b}{T} + c\right)P + \left(\frac{d}{T^2} + \frac{e}{T} + f\right)\frac{P^2}{2} \tag{B.16}$$

where P is the total gas pressure (vapor and CO_2), T is absolute temperature, and a, b, c, d, e, and f are constants fitted from experimental data. For P-T ranges, 50-350°C, up to 500 bars, the fitted constants for CO_2 have the following values: a = -1430.87, b = 3.598, c = -2.27376×10⁻³, d = 3.47644, e = -1.04247×10⁻², and f = 8.36271×10⁻⁶. Examples of equilibrium calculations between aqueous and gas phases show that ideal mixing of real gases is a reasonable approximation near the water saturation pressure curve (Spycher and Reed, 1988). Details on fugacity correction are given in Section H.4 of Appendix H.

For low ionic strength solution, the CO_2(aq) activity coefficient γ can be assumed equal to one. For a high ionic strength sodium chloride solution, γ should be corrected (salting out effect). Here we use an activity coefficient expression of Drummond (1981) for CO_2(aq):

$$\ln \gamma = \left(C + FT + \frac{G}{T}\right)I - (E + HT)\left(\frac{I}{I+1}\right) \tag{B.17}$$

where T is the absolute temperature, I is ionic strength (or sodium chloride molality), C, F G, E, and H are constants (C=-1.0312, F=0.0012806, G=255.9, E=0.4445, and H=-0.001606). A similar expression is used in other geochemical modeling codes such as in EQ3/6 (Wolery, 1992). The ionic strength, I, is defined by

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{B.18}$$

where the summation is over all aqueous species, and c_i and z_i are concentration (mol/kg H_2O) and electrical charge of species i.

B.6 Cation exchange

Cation exchange takes place when free cations in solution exchange with interlayer cations. This process can be described as an equilibrium reaction between an exchangeable cation and an exchange site. The equilibrium constant is usually known as the exchange coefficient because its value depends on the ionic strength of the solution. A general expression for cation exchange reactions according to the Gaines-Thomas convention is (Appelo and Postma, 1993):

$$\frac{1}{v_i}S_i + \frac{1}{v_j}\left(X_{v_j} - S_j\right) \Leftrightarrow \frac{1}{v_i}\left(X_{v_i} - S_i\right) + \frac{1}{v_j}S_j \tag{B.19}$$

where v_i and v_j are the stoichiometric coefficients (equal to their charges) of dissolved and interlayer cations, respectively; S_i and S_j denote dissolved cationic species and $\left(X_{v_i} - S_i\right)$ and $\left(X_{v_j} - S_j\right)$ represent exchange sites or exchange interlayer cations. Let's have an example:

$$Na^+ + 0.5Ca\text{-}X_2 = 0.5Ca^{2+} + Na\text{-}X \tag{B.19a}$$

$$Na^+ + K\text{-}X = K^+ + Na\text{-}X \tag{B.19b}$$

The equilibrium equation for cation exchange is obtained from the Mass Action Law:

$$K_{ij}^* = \frac{\overline{w_i}^{-1/v_i} \cdot a_j^{1/v_j}}{\overline{w_j}^{-1/v_j} \cdot a_i^{1/v_i}} \tag{B.20}$$

where K_{ij}^* is the exchange coefficient or selectivity, a_j is the activity of the j-th dissolved species and $\overline{w_i}$ is the activity of the i-th interlayer cation. For the example of (B.19a), we have:

$$K_{Na/Ca}^* = \frac{\overline{w}_{Na} \cdot a_{Ca}^{0.5}}{\overline{w}_{Ca}^{0.5} \cdot a_{Na}} \tag{B.20a}$$

Activities of dissolved cations are related to concentrations as given in Appendix H. Activities of interlayer cations are approximated by (1) their equivalent fractions of the number of exchange sites, which is commonly referred as the **Gaines-Thomas** convention (Appelo and Postma, 1993), after Gaines and Thomas (1953) who was among the first to give a rigorous definition of a thermodynamic standard state of interlayer

cations; or (2) their molar fractions of the number of exchange sites, which follows **Vanselow** convention (Vanselow, 1932). Thus, the activity of the interlayer cation $\overline{w_i}$ is assumed to be equal to its fraction β_i of equivalent (Gaines-Thomas convention) or mole (Vanselow convention), and is calculated as:

$$\overline{w_i} \cong \beta_i = \frac{w_i}{\sum\limits_{i=1}^{N_w} w_i} \tag{B.21}$$

where w_i is the concentration of the i-th interlayer cation and N_w is the total number of such interlayer cations. The sum of concentrations of exchange sites or interlayer cations is the so-called cation exchange capacity (CEC). Substituting (B.21) into (B.20) yields the general equation for cation exchange:

$$K_{ij}^* = \frac{\beta_i^{1/v_i} \cdot \left(c_j \gamma_j\right)^{1/v_j}}{\beta_j^{1/v_j} \cdot \left(c_i \gamma_i\right)^{1/v_i}} \tag{B.22}$$

where the activity of each dissolved species a_i has been expressed as the product of its concentration c_i time its activity coefficients γ_i. The Na/Ca exchange example becomes

$$K_{Na/Ca}^* = \frac{\beta_{Na}^{1/1} \cdot \left(c_{Ca} \gamma_{Ca}\right)^{1/2}}{\beta_{Ca}^{1/2} \cdot \left(c_{Na} \gamma_{Na}\right)^{1/1}} \tag{B.22a}$$

From Eq. (B.22), β_j can be expressed as

$$\beta_j = \left(K_{ij}^*\right)^{-v_j} c_j \gamma_j \left(\frac{\beta_i}{c_i \gamma_i}\right)^{v_j/v_i} \qquad j = 1,2,\cdots,N_w \tag{B.23}$$

For Na/Ca exchange example, we have:

$$\beta_{Ca} = \left(K_{Na/Ca}^*\right)^{-2} c_{Ca} \gamma_{Ca} \left(\frac{\beta_{Na}}{c_{Na} \gamma_{Na}}\right)^{2/1} \tag{B.23a}$$

From the definition of Eq. (B.21), one has:

$$\sum_{j=1}^{N_w} \beta_j = 1 \tag{B.24}$$

Substituting Equation B.23 into B.24 results in:

$$\sum_{j=1}^{N_w}\left(K_{ij}^*\right)^{-\nu_j}c_j\gamma_j\left(\frac{\beta_i}{c_i\gamma_i}\right)^{\nu_j/\nu_i}=1 \tag{B.25}$$

which for given dissolved concentrations cj can be solved for the single unknown β_i. This equation is quadratic when cation exchange involves only homovalent and divalent cations. However, when cation exchange involves also trivalent cations a cubic equation is obtained. Once the equivalent fraction β_i is known the rest of exchange fractions can be calculated from Equation B.21. According to Equation B.21, the concentration of the i-th exchanged cation w_j (in moles per liter of fluid) can be obtained from

$$w_j=\beta_j\sum_{j=1}^{N_w}w_j\,\rho_s\,\frac{(1-\phi)}{100\phi z_j}\qquad \text{for \textit{Gaines-Thomas} convention} \tag{B.26a}$$

$$w_j=\beta_j\sum_{j=1}^{N_w}w_j\,\rho_s\,\frac{(1-\phi)}{100\phi}\qquad \text{for \textit{Vanselow} convention} \tag{B.26b}$$

For the commonly used Gaines-Thomas convention, $\sum_{j=1}^{N_w}w_j$ is also referred as CEC, the cation exchange capacity (usually measured as the number of milli equivalents of cations per 100 gram of solid), ϕ is the porosity, ρ_s is the density of the solids (kg of solids per dm³ of solids), and z_j is the cation charge.

A third cation exchange convention implemented is **Gapon** convention (Gapon, 1933). In this convention, the activities of the adsorbed ions are expressed as a fraction of the number of exchange sites (X⁻). When cation exchange involves homovalent and divalent cations, the reaction should be written as

$$Na^+ + Ca_{0.5}\text{-}X = 0.5Ca^{2+} + Na\text{-}X \tag{B.27}$$

with

$$K_{Na/Ca}^*=\frac{[Na-X][Ca^{2+}]^{0.5}}{[Ca_{0.5}-X][Na^+]}=\frac{\beta_{Na}[Ca^{2+}]^{0.5}}{\beta_{Ca}[Na^+]} \tag{B.28}$$

In this case, molar and equivalent fractions become identical since both are based on a single exchange site with charge -1.

Under variably water-saturated condition, exchangeable surface sites depend on water saturation. Assuming an ideal-wetting condition, using a correct with water saturation S_l, Eq. B.26a becomes (a similar form for B.26b):

$$w_j = \beta_j \sum_{j=1}^{N_w} w_j \, \rho_s \, \frac{(1-\phi)}{100\phi z_j S_l}$$

(B.29)

In Eq. B.29, as S_l goes to zero, the surface sites (concentration) would tend to infinity. Clearly, at a very low liquid saturation, the exchangeable (reactive or effective) sites of the soil contacted by water are likely much smaller than the total sites.

The dependence of the surface sites on water saturation is very complex in field-scale conditions. Two methods (models) have been implemented to address this phenomenon. The first method considers that the surface sites contacted by water diminish proportionately to the saturation (Model 1), or ideal-wetting condition. The second method considers multiplying a (correction) factor f that depends on liquid saturation, $f(S_l)$, or

$$w_j = \beta_j \sum_{j=1}^{N_w} w_j \, \rho_s \, \frac{(1-\phi)}{100\phi z_j S_l} f(S_l)$$

(B.30)

Values of the factor f range from zero to one, or $0 \le f \le 1$. One $f(S_l)$ function could be adopted from the reactive surface area calculations for dissolution and precipitation of minerals (Model 2; see Appendix K).

The above equations (B.19 to B.30) are formulated for a single-site exchange of cations. Multi-site exchanges are implemented. Each site is assumed to be independent. Eqs. B.19 to B.30 are applied for each site.

B.7   Surface Complexation

Surface Electric Potential Model

The sorption of solutes on solid surfaces can be described as a chemical reaction between the aqueous species and the specific surface sites (surface complexation). These surface reactions include proton exchange, cation binding and anion binding via ligand exchange at surface hydroxyl sites (represented here as XOH to avoid confusion with other chemical species). For example, the sorption of a metal could be represented as:

$$XOH + M^{z_+} = XOM^{z_{+-1}} + H^+$$

(B.31)

At equilibrium, the sorption reactions can be described by the mass law equation:

$$K_{app} = \frac{\left[XOM^{z_+^{-1}} \right] a_{H^+}}{\left[XOM \right] a_{M^{z+}}}$$

(B.32)

where K_{app} is referred to as the apparent equilibrium constant, because it includes surface charge effects and hence is dependent on the extent of surface ionization (Dzombak and Morel, 1990), a is the thermodynamic activity of the aqueous species, and the terms in brackets represent the concentration of surface complexes (mol/kg).

In aqueous complexation reactions, the electric charge is assumed to be homogeneous in the solution. However, surface reactions take place on a fixed charged surface creating an electrostatic field. An additional energetic term accounting for the work needed for the aqueous species to travel across the surface electric field is required:

$$\Delta G_{ads} = \Delta G_{intr} + \Delta G_{coul} = \Delta G_{intr} + (\Delta G_{\psi=0} - \Delta G_{\psi=\psi_0}) = \Delta G_{intr} - zF\psi_0$$

(B.33)

where ΔG_{ads} is the free enthalpy change of the overall adsorption reaction, $\Delta G_{int\,r}$ and ΔG_{coul} are the free enthalpy change due to chemical bonding and to the electrostatic work, respectively, z is the charge of the surface species, F the Faraday's constant (96485 C/mol), and ψ_0 is the mean surface potential (V). Since

$$\Delta G = -RTlnK$$,

(B.34)

Equation (B.33) can be rewritten as:

$$K_{app} = K_{int}\, e^{\frac{zF\psi_0}{RT}}$$,

(B.35)

where R is the gas constant (8.354 J/mol/K), T is the absolute temperature (K), and K_{int} is the intrinsic equilibrium constant which does not depend on the surface charge.

Diffuse Layer Model

The diffuse layer model has been described in great detail by Dzombak and Morel (1990) and was applied to adsorption of metals on iron oxide surfaces. In the diffuse layer model, the solid-water interface is composed of two layers: a layer of surface-bound complexes and a diffuse layer of counter ions in solution. The surface charge is calculated from the total surface species adsorbed on the layer:

$$\sigma_p = \frac{F}{A} \sum_{k=1}^{N_s} z_k\, y_k$$

(B.36)

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According to the Gouy-Chapman theory, the surface charge density σ_p (c/m²) is related to the potential at the surface (volt) by:

$$\sigma_d = (8RT\varepsilon\varepsilon_0 I \times 10^3)^{1/2} \sinh(zF\psi_0/2RT),$$
(B.37)

where R is the molar gas constant (8.354 J mol-1 K-1), T is the absolute temperature (K), is the relative dielectric constant of water (ε = 78.5 at 29oC), ε_0 is the permittivity of free space (8.754 10-12 C V-1 m-1 or 8.754 10-12 C2 J-1 m-1), and C is the molar electrolyte concentration (M). Equation (B.37) is only valid for a symmetrical electrolyte (Z=ionic charge). It is common to use the linearized version of Equation (B.37) for low values of the potential:

$$\sigma_p = \varepsilon\varepsilon_0\kappa\psi_0,$$
(B.38)

where 1/κ (m) is the double-layer thickness defined as:

$$\frac{1}{\kappa} = \left(\frac{\varepsilon\varepsilon_0 RT}{2F^2 \cdot 1000I}\right)^{1/2}$$
(B.39)

Equations (B.37) can be simplified by rewritten $(8RT\varepsilon\varepsilon_0 I \times 10^3)^{1/2}$ for 29°C:

$$\sigma_p = 0.1174 I^{1/2} \sinh(zF\psi_d/2RT)$$
(B.40)

Therefore, in the diffuse-layer model, the value of the capacitance C relating the surface charge and the potential can be calculated based on theoretical considerations (Equation B.38) instead of being an experimental fitting parameter.

Constant Capacitance Model

Similar to the diffused-layer, the constant capacitance model is based on the assumption that all the species are adsorbed in the same layer and a diffuse layer of counterions constitutes the transition to homogenous solution. However, differently from the diffuse-layer model, the relationship between the surface charge and the potential is assumed to be linear:

$$\sigma = C\psi$$
(B.41)

where C is a constant value to be obtained from fitting experimental data.

Mathematical Formulation of Adsorption Reactions

Lets us consider the following surface desorption reaction:

$$XOM^{z_+ -1} = XOH + M^{z_+} - H^+$$

with the equilibrium constant of the reaction given as:

$$K_{int} = \frac{[XOH]a_M}{[XOM]a_{H^+}} e^{\left(\frac{-zF\psi_0}{RT}\right)}$$

(B.42)

Usually, the neutral surface complex *XOH* is included in the N_C aqueous primary species. The new unknown is the potential term

$$\tilde{\psi} = \frac{-F\psi_0}{RT}$$

(B.43)

The concentration of a surface complex, y_j, (mol/m³), can be expressed in terms of the concentration of the primary species and the potential term:

$$y_j = K_j^{-1} \prod_{i=1}^{N_C} c_i^{v_{ji}^y} \gamma_i^{v_{ji}^y} e^{z_j \tilde{\psi}} \qquad j = 1...N_Y$$

(B.44)

where K_j is the intrinsic equilibrium constant of the desorption reaction.

In order to solve for the potential term, an additional equilibrium equation is needed. For the double diffuse layer model, we obtain Equation (B.45), if the Guoy-Chapman double-layer theory is used to relate surface charge and the potential (Equation (B.37)). If the linearized Equation (B.38) is used, we obtain Equation (B.46). If a constant capacity model is used, we obtain Equation (B.47).

$$(8RT\varepsilon\varepsilon_0 I \times 10^3)^{1/2} \sinh(-\tilde{\psi}/2) - \frac{F}{A}\sum_{k=1}^{N_s} z_k\, y_k = 0$$

(B.45)

$$\frac{F^2}{A\varepsilon\varepsilon_0 \kappa RT}\sum_{k=1}^{N_s} z_k\, y_k + \tilde{\psi} = 0$$

(B.46)

$$\frac{F^2}{ACRT}\sum_{k=1}^{N_s} z_k\, y_k + \tilde{\psi} = 0$$

(B.47)

Appendix C Solution Method for Solute Transport Equations

Most chemical species are only subject to transport in the liquid phase. A few species can be transported in both liquid and gas phases such as O_2 and CO_2. We first derive the numerical formulation of reactive transport in the liquid phase. This will then be extended to transport in the gas phases for some gaseous species.

C.1   Transport in the Liquid Phase

In the sequential iteration approach (SIA), the mass transport equations and chemical reaction equations are considered as two relatively independent subsystems. They are solved separately in a sequential manner following an iterative procedure. If reactions taking place in the liquid phase are assumed to be at local equilibrium, mass transport equations can be written in terms of total dissolved component concentrations. By lumping all mass accumulation terms due to mass transfer between aqueous and solid phases including precipitated (kinetics and equilibrium), exchanged and sorbed species, and by using Equation (4.1) (in Chapter 4), we can write equations for multi-component chemical transport in the liquid phase as

$$\frac{\Delta t}{V_n} \sum_m A_{nm} \left[u_{nm}^{k+1} C_{nm}^{(j),k+1,s+1/2} + D_{nm} \frac{C_m^{(j),k+1,s+1/2} - C_n^{(j),k+1,s+1/2}}{d_{nm}} \right] =$$

$$\Delta M_n^{(j),k+1} - q_n^{(j)k+1}\Delta t - R_n^{(j),k+1,s}\Delta t \qquad j = 1,2,..., \ N_C \tag{C.1}$$

where n labels the grid block, m label the adjacent grid blocks connected to n, j labels the chemical component, N_C is the total number of chemical components, l labels liquid phase (for simplicity, the liquid phase index l is neglected), k labels the number of the time step, s labels the number of the transport-chemistry iteration (details is given later), u_{nm} is the liquid volumetric flux or the Darcy velocity (m/s), D_{nm} is the effective diffusion coefficient (including effects of porosity, phase saturation, tortuosity and weighting factors between the two grid blocks), d_{nm} is the nodal distance, $R_n^{(j)k+1}$ are the overall chemical reaction source/sink terms.

The concentrations in the advective and diffusive flux terms of Equation (C.1) can be evaluated by

$$C_{nm}^{(j),k+1,s+1/2} = \theta \left[\varepsilon_{nm} C_n^{(j),k+1,s+1/2} + (1-\varepsilon_{nm})C_m^{(j),k+1,s+1/2} \right]$$
$$(1-\theta)\left[\varepsilon_{nm} C_n^{(j),k} + (1-\varepsilon_{nm})C_m^{(j),k} \right]$$

$$\tag{C.2}$$

$$C_n^{(j),k+1,s+1/2} = \theta C_n^{(j),k+1,s+1/2} + (1-\theta)C_n^{(j),k}$$

$$C_m^{(j),k+1,s+1/2} = \theta C_m^{(j),k+1,s+1/2} + (1-\theta)C_m^{(j),k}$$

where θ is the time weighting factor, with values in the range from 0 to 1; θ = 1 indicates a fully implicit calculation; and

$$\varepsilon_{nm} = \begin{cases} 0 & \text{if} \quad u_{nm} \geq 0 \quad \text{inflow} \\ 1 & \quad\quad u_{nm} < 0 \quad \text{outflow} \end{cases}$$

Fully upstream weighting is used for advective flux calculations. The mass accumulation terms can be evaluated as

$$\Delta M_n^{(j),k+1} = S_{l,n}^{k+1} \phi_n^{k+1} C_n^{(j),k+1,s+1/2} - S_{l,n}^{k} \phi_n^{k} C_n^{(j),k}$$

(C.3)

By substituting Equations (C.2) and (C.3) into (C.1), and then rearranging them in terms of unknowns, $C^{(j),k+1,s+1/2}$ (total dissolved component concentrations), one has

$$\left[S_{l,n}^{k+1} \phi_n^{k+1} + \frac{\theta \Delta t}{V_n} \sum_m A_{nm} \left(-u_{nm}^{k+1} \varepsilon_{nm} + \frac{D_{nm}}{d_{nm}} \right) \right] C_n^{(j),k+1,s+1/2} +$$

$$\frac{\theta \Delta t}{V_n} \sum_m A_{nm} \left[u_{nm}^{k+1} (\varepsilon_{nm} - 1) - \frac{D_{nm}}{d_{nm}} \right] C_m^{(j),k+1,s+1/2} \quad\quad =$$

$$\frac{(1-\theta)\Delta t}{V_n} \sum_m A_{nm} \left(u_{nm}^{k+1} \varepsilon_{nm} - \frac{D_{nm}}{d_{nm}} \right) C_n^{(j),k} -$$

$$\frac{(1-\theta)\Delta t}{V_n} \sum_m A_{nm} \left[u_{nm}^{k+1} (\varepsilon_{nm} - 1) + \frac{D_{nm}}{d_{nm}} \right] C_m^{(j),k}$$

$$S_{l,n}^{k} \phi_n^{k} C_n^{(j),k} + q_n^{(j)k+1} \Delta t + R_n^{(j),k+1,s} \Delta t \quad\quad\quad j = 1,2,...,N_C$$

(C.4)

For the sequential iteration approach, the iteration index s is essential. A new transport-chemistry iteration consists of two parts, transport part denoted by, s+1/2, (it should be noted that ½ does not mean Δt/2), and chemistry part denoted by, s+1. Equation (C.4) for each chemical component j is linear if $R^{(j),s}$ is known, and has the same structure as the non-reacting (conservative) solute transport equation. The chemical reaction source/sink term $R^{(j),s}$ represents mass transfer of component j between aqueous and solid phases. The values of these source/sink terms at the new transport iteration, s+1/2, are evaluated at the previous chemistry iteration, s. The resulting new values of $C^{(j),s+1/2}$, obtained by solving transport Equations (C.1), are substituted into chemical reaction subroutines and one can compute new values of $R^{(j),s+1}$. Transport and chemical reaction equations are solved iteratively until the prescribed convergence criteria are satisfied. The essence of this sequential iteration approach is therefore the sequential solution of two independent sets of equations: the transport equations and the chemical equations. The transport equations are solved on a component-by-component basis, whereas the chemical equations are solved on a grid block by grid block basis. These two sets of equations are coupled by updating chemical source/sink terms.

For kinetic mineral dissolution-precipitation, the terms $R^{(j)}$ can be calculated directly from kinetic expressions. For equilibrium, these terms can be obtained indirectly from component mass balance equations. The solution of chemical equilibrium system and calculation of the source/sink terms $R^{(j)}$ are presented in Appendix D. From the chemistry point of view, equilibrium mineral dissolution-precipitation does not appear in an explicit rate expression. To avoid confusion, we write the last term in Equation (C.4) as

$$R_n^{(j),k+1,s}\Delta t = -\Delta P_n^{(j),k+1,s}$$

(C.5)

where $\Delta P_n^{(j),k+1,s}$ means mass transfer of component j from the aqueous phase to the mineral phase at iteration s, grid block n and time step k+1 (or called mass accumulation in mineral phases; negative values indicate mass transfer from the mineral phase to the aqueous phase).

Returning to Equation (C.4), we can see that the coefficient matrix is the same for all chemical components as long as diffusion coefficients are the same for all aqueous species. The matrix depends on space and time discretization, and flow conditions. The equations for different components only differ in right-hand side terms.

The mathematical treatment of adding Kd linear adsorption and first-order decay effects in the model follows the work by Oldenburg and Pruess (1995, EOS7R), but no gas phase partitioning is considered. The mass accumulation term for any species (for simplification, the species index is not appeared in the following equations) with Kd adsorption on the solid matrix is

$$M = \phi S_l C + (1-\phi)\rho_s C K_d$$

(C.6)

where ϕ is porosity, S_l is the liquid saturation, C is the aqueous concentration (mol/l), ρ_s is the solid density (kg/dm³), K_d is the distribution coefficient (l/kg = mass/kg solid divided by mass/l solution) and is species-dependent. The accumulation also term can be written in terms of a retardation factor

$$M = \phi S_l R C$$

(C.7)

and

$$R = 1 + \frac{(1-\phi)\rho_s}{\phi S_l} K_d$$

(C.8)

The input can be optionally by Kd and R, depending on user convenience and data availability.

The first-order decay of a species is handled by the discretized equation (Oldenburg and Pruess, 1995)

$$M_n^{k+1}(1+\lambda\Delta t) - M_n^k = \frac{\Delta t}{V_n}\left(\sum_m A_{nm}F_{nm}^{k+1} + V_n q_n^{k+1}\right) \qquad (C.9)$$

where λ is decay constant (1/s) which is species-dependent, subscript n labels grid block, superscript k labels time step, subscript m labels the grid block connected to grid block n, Δt is time step size, M_n is the average mass per unit volume, surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}, F_{nm} is the average mass flux over the surface segment A_{nm} between volume elements V_n and V_m, and q is the average value of source/sink term per unit volume and unit time.

C.2   Transport in the Gas Phase

Gaseous species concentrations can be related to partial pressures by

$$C_g = \frac{10^2}{RT}P_g \qquad (C.10)$$

where C_g are gaseous species concentrations (in mol/l), P_g is the gaseous species partial pressure (in bar), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. By following the same principle as used for transport in liquid phase and by considering Equation (C.10), the numerical formulation of gaseous transport in the gas phases can be expressed as

$$\left[\frac{10^2}{RT}S_{g,n}^{k+1}\phi_n^{k+1} + \frac{\Delta t}{V_n}\sum_m A_{nm}\frac{10^2}{RT}\left(-u_{g,nm}^{k+1}\varepsilon_{g,nm} + \frac{D_{g,nm}}{d_{nm}}\right)\right]P_{g,n}^{(j),k+1,s+1/2} +$$

$$\frac{\Delta t}{V_n}\sum_m A_{nm}\frac{10^2}{RT}\left[u_{g,nm}^{k+1}(\varepsilon_{g,nm}-1) - \frac{D_{g,nm}}{d_{nm}}\right]P_{g,m}^{(j),k+1,s+1/2} = \qquad (C.11)$$

$$\frac{10^2}{RT}S_{g,n}^k\phi_n^k P_{g,n}^{(j),k} + q_n^{(j)k+1}\Delta t + R_n^{(j),k+1,s}\Delta t \qquad\qquad j = 1,2,...,N_g$$

where N_g is number of gaseous species. The structure of Equations (C.11) is the same as that of (C.4) for transport only in liquid phase. The same solution method can be applied for solving Equations (C.11).

Appendix D Solution Method for Mixed Equilibrium-Kinetics Chemical System

Aqueous complexation and gas dissolution/exsolution proceed according to local equilibrium, while mineral dissolution/precipitation are subject to equilibrium and/or kinetic conditions. Gas dissolution/exsolution is included in the model and treated in a similar way as equilibrium mineral dissolution/precipitation but fugacity correction. The formulation is based on mass balances in terms of basis species as used by Parkhurst el al. (1980) and Reed (1982) for the equilibrium chemical system. The kinetic

rate expressions for mineral dissolution/precipitation are included in the equations along with the mass balances of basis species. At time zero (initial), the total concentrations of basis species j in the system are assumed to be known, and are given by

$$T_j^0 = c_j^0 + \sum_{k=1}^{N_x} \nu_{kj} c_k^0 + \sum_{m=1}^{N_p} \nu_{mj} c_m^0 + \sum_{n=1}^{N_q} \nu_{nj} c_n^0 + \sum_{z=1}^{N_z} \nu_{zj} c_z^0 + \sum_{s=1}^{N_s} \nu_{sj} c_s^0 \qquad j = 1...N_C \qquad \text{(D.1)}$$

where superscript 0 represents time zero; c denotes concentration; subscripts j, k, m, n, z and s are the indices of the primary species, aqueous complexes, minerals at equilibrium, minerals under kinetic constraints, and exchanged and surface complexes, respectively; N_c, N_x, N_p, N_q, N_z and N_s are the number of corresponding species and minerals; and ν_{kj}, ν_{mj}, ν_{nj}, ν_{zj} and ν_{sj} are stoichiometric coefficients of the primary species in the aqueous complexes, equilibrium, kinetic minerals, and exchanged and surface complexes, respectively.

After a time step Δt, the total concentration of primary species j (T_j) is given by

$$T_j = c_j + \sum_{k=1}^{N_x} \nu_{kj} c_k + \sum_{m=1}^{N_p} \nu_{mj} c_m + \sum_{n=1}^{N_q} \nu_{nj} \left(c_n^0 - r_n \Delta t \right) + \sum_{z=1}^{N_z} \nu_{zj} c_z + \sum_{s=1}^{N_s} \nu_{sj} c_s \qquad j = 1...N_C$$

$$\text{(D.2)}$$

where r_n is the kinetic rate of mineral dissolution (negative for precipitation, units used here are mole per kilogram of water per time), for which a general multi-mechanism rate law can be used. Δt and T_j are related through generation of j among primary species as follows

$$T_j - T_j^0 = \sum_{l=1}^{N_a} \nu_{lj} r_l \Delta t \qquad j = 1,...N_C \qquad \text{(D.3)}$$

where l is the aqueous kinetic reaction (including biodegradation) index, N_a is total number of kinetic reactions among primary species, and r_l is the kinetic rate which is in terms of one mole of product species.

By substituting Equations (D.1) and (D.2) into Equation (D.3), and denoting residuals as F_j^c (which are zero in the limit of convergence), we have

$$
\begin{aligned}
F_j^c = \ & (c_j - c_j^0) && \text{primary species} \\
& + \sum_{k=1}^{N_x} \nu_{kj}(c_k - c_k^0) && \text{equilibriu m aqueous complexes} \\
& + \sum_{z=1}^{N_z} \nu_{zj}(c_z - c_z^0) && \text{exchanged complexes} \\
& + \sum_{s=1}^{N_s} \nu_{sj}(c_s - c_s^0) && \text{surface complexes} \\
& + \sum_{m=1}^{N_p} \nu_{mj}(c_m - c_m^0) && \text{equilibriu m minerals} \\
& - \sum_{n=1}^{N_q} \nu_{nj} r_n \Delta t && \text{kinetic minerals} \\
& - \sum_{l=1}^{N_a} \nu_{lj} r_l \Delta t && \text{kinetics among primary species} \\
= \ & 0 && j = 1 \ldots N_C
\end{aligned}
$$

(D.4)

According to mass-action equations, the concentrations of aqueous and exchanged complexes ck and cz can be expressed as functions of concentrations of the primary species cj. Kinetic rates rn and rl are functions of cj. The expression for rn is given in Eq. B.6 in Appendix B, and rl will be presented in Eq. B.2. Surface complexes are expressed as the product of primary species and an additional potential term Ψ. Additional equilibrium equations (Equation (B.42) or (B.43)) depending on the surface complexation model have to be solved together with Equation (D.4). No explicit expressions relate equilibrium mineral concentrations cm to cj. Therefore, NP additional mass action equations (one per mineral) are needed, which are provided by Equation (B.5). At equilibrium we have the residual functions

$$
F_m^p = SI_m = 0 \qquad m = 1, \ldots, N_P
$$

(D.5)

where SI_m is the m-th equilibrium mineral saturation index which is a function of c_j (see Equations B.4 and B.5 in Appendix B). N_C equations in (D.4) and N_p in (D.5) constitute a complete set of equations needed for $N_C + N_P$ primary variables, $(c_1, c_2, \ldots, c_{N_C}, c_1, c_2, \ldots, c_{N_p})$. Denoting the set of primary variables collectively as X_i (i=1, 2, …, $N_C + N_P$), using Newton-Raphson iteration we have

$$
\sum_{i=1}^{N_C + N_P} \frac{\partial F_j}{\partial X_i} \Delta X_i = - F_j \qquad j = 1, \ldots, N_C + N_P
$$

(D.6)

where j is a row index and i is a column index (here j as a row index can be thought of as also representing an "extended" basis set including the equilibrium minerals). In matrix form Eqs. (D.6) reduce to

$$
J \Delta X = - F
$$

(D.7)

where $\mathbf{J}$ is the so-called Jacobian matrix. The matrix elements are evaluated in Appendix E. The values of are used to update the primary variables:

$$X_i^{s+1} = X_i^s + \Delta X_i^s$$

<div align="right">(D.8)</div>

where s labels iteration number. The $|\Delta X_i|$ are expected to decrease in successive iterations. The system of equations is considered satisfactorily solved when

$$\max_j \left(\frac{|F_j^c|}{T_j^0} \right) \leq \tau \qquad j = 1, \, ..., \, N_C$$

<div align="right">(D.9)</div>

where τ is specified tolerance limit. In order to avoid negative values for concentrations of the basis species, the relative change is restricted to one (called under-relaxation), or $\dfrac{|\Delta x_i|}{x_i} < 1 \quad i = 1... N_C + N_P + N_S$ (

$i = 1...N_C$). As a consequence, although the iteration method becomes more robust, the rate of convergence may slow down in some cases. When a negative value of X_i $(i = N_C + 1, ..., N_C + N_p)$ is obtained, the corresponding mineral is considered exhausted and must be removed from the chemical system, and its corresponding equation disappears (Reed, 1982). In this case, the speciation in solution may change drastically. This might have a strong effect on kinetic rate laws. So when a change occurs in the mineral assemblage, one might have to limit the time step to retain accuracy in rate law integration. In addition, for a given time step the code checks that dissolution of a mineral cannot be greater than the amount present in the medium, in order to avoid "over-dissolution".

The solution of the reaction system requires knowing initial total concentrations of basis species j in the equilibrium system (aqueous and mineral), and the time step Δt_r. Adding kinetic mineral dissolution/precipitation processes does not require additional primary equations, because the reaction rate is a function of the concentrations of the basis species. Once the concentrations of the basis species are obtained, all other secondary variables can be computed in a straightforward manner.

Appendix E   Evaluation of the Jacobian Matrix for the Chemical Equations

The final Jacobian matrix has *Nc+Np+* rows and *Nc+Np+* columns, as follows:

$$
\begin{array}{cccc}
 & Nc & Np & N\psi \\[6pt]
Nc & \dfrac{\partial F_j^c}{\partial c_i} & \dfrac{\partial F_j^c}{\partial p_i} & \dfrac{\partial F_j^c}{\partial \tilde{\psi}} \\[12pt]
Np & \dfrac{\partial F_j^p}{\partial c_i} & \dfrac{\partial F_j^p}{\partial p_i} & \dfrac{\partial F_j^p}{\partial \tilde{\psi}} \\[12pt]
N\psi & \dfrac{\partial F^{\tilde{\psi}}}{\partial c_i} & \dfrac{\partial F^{\tilde{\psi}}}{\partial p_i} & \dfrac{\partial F^{\tilde{\psi}}}{\partial \tilde{\psi}}
\end{array}
\tag{E.1}
$$

The entries of the Jacobian matrix are

$$
J^{cc} = \frac{\partial F_j^c}{\partial c_i} = \delta_{ji} + \sum_{k=1}^{N_x} v_{kj} v_{ik} \frac{c_k}{c_i} + \sum_{n=1}^{Nq} v_{nj} v_{in} \frac{k_n A_n \Omega_n}{c_i} + \sum_{s=1}^{Ns} v_{sj} v_{is} \frac{c_s}{c_i}
\tag{E.2}
$$

$$
\mathbf{J}^{cp} = \frac{\partial \mathrm{F}_j^c}{\partial \mathrm{p}_i} = v_{mj}
\tag{E.3}
$$

$$
\mathbf{J}^{pc} = \frac{\partial \mathrm{F}_j^p}{\partial \mathrm{c}_i} = \frac{v_{mj}}{c_i}
\tag{E.4}
$$

$$
J^{pp} = \frac{\partial F_j^p}{\partial p_i} = 0
\tag{E.5}
$$

$$
J^{c\tilde{\psi}} = \frac{\partial F_j^c}{\partial \tilde{\psi}} = \sum_{s=1}^{Ns} v_{sj} z_s c_s
\tag{E.6}
$$

$$
J^{\tilde{\psi}c} = \frac{\partial F^{\tilde{\psi}}}{\partial c_i} = -\sum_{s=1}^{N_s} z_s v_{is} \frac{c_s}{c_i}
\tag{E.7}
$$

or

$$
J^{\tilde{\psi}c} = \frac{\partial F^{\tilde{\psi}}}{\partial c_i} = \frac{F^2}{A\varepsilon\varepsilon_0 \kappa RT} \sum_{s=1}^{N_s} z_s v_{is} \frac{c_s}{c_i}
\tag{E.8}
$$

or

$$
J^{\tilde{\psi}c} = \frac{\partial F^{\tilde{\psi}}}{\partial c_i} = \frac{F^2}{ACRT} \sum_{s=1}^{N_s} z_s v_{is} \frac{c_s}{c_i}
\tag{E.9}
$$

$$
J^{\tilde{\psi}\tilde{\psi}} = \frac{\partial F^{\tilde{\psi}}}{\partial \tilde{\psi}} = -\tfrac{1}{2}(8RT\varepsilon\varepsilon_0 I \times 10^3)^{1/2} \cosh(-\tilde{\psi}/2) - \frac{F}{A}\sum_{k=1}^{N_s} z_k z_k y_k
\tag{E.10}
$$

or

$$J^{\tilde{\psi}\tilde{\psi}} = \frac{\partial F^{\tilde{\psi}}}{\partial \tilde{\psi}} = \frac{F^2}{A\varepsilon\varepsilon_0\kappa RT} \sum_{s=1}^{N_s} z_s z_s c_s + 1 \qquad \text{(E.11)}$$

or

$$J^{\tilde{\psi}\tilde{\psi}} = \frac{\partial F^{\tilde{\psi}}}{\partial \tilde{\psi}} = \frac{F^2}{ACRT} \sum_{s=1}^{N_s} z_s z_s c_s + 1 \qquad \text{(E.12)}$$

Appendix F Effects of Mineral Precipitation/Dissolution on Hydrologic Properties

F.1 Porosity Changes

Porosity changes in matrix and fractures are directly tied to the volume changes as a result of mineral precipitation and dissolution. The molar volumes of minerals created by hydrolysis reactions (i.e., anhydrous phases, such as feldspars, reacting with aqueous fluids to form hydrous minerals such as zeolites or clays) are often larger than those of the primary reactant minerals; therefore, constant molar dissolution-precipitation reactions may lead to porosity reductions. Porosity changes are taken into account in the code as follows:

The porosity of the medium (fracture or matrix) is given by

$$\phi = 1 - \sum_{m=1}^{nm} fr_m - fr_u \qquad \text{(F.1)}$$

where nm is the number of minerals, fr_m is the volume fraction of mineral m in the rock ($V_{mineral}/V_{medium}$, including porosity), and fr_u is the volume fraction of nonreactive rock. As the fr_m of each mineral changes, the porosity is recalculated at each time step. The porosity is not allowed to go below zero.

Several options are available in TOUGHREACT to compute permeability changes as a result of mineral precipitation and/or dissolution. Some options depend solely on porosity changes, whereas others employ options related to, for example, fracture aperture changes or pore throat diameter changes.

F.2 Fracture Permeability Changes

Option 3: Fracture permeability changes can be approximated using the porosity change and an assumption of plane parallel fractures of uniform aperture (cubic law; e.g., Steefel and Lasaga, 1994). The modified permeability, k, is then given by

$$k = k_i \left(\frac{\phi}{\phi_i} \right)^3 \qquad \text{(F.2)}$$

where k_i and ϕ_i are the initial permeability and porosity, respectively. This law yields zero permeability only under the condition of zero fracture porosity.

Option 4: In most experimental and natural systems, permeability reductions to values near zero occur at porosities significantly greater than zero. This generally is the result of mineral precipitation in the narrower interconnecting apertures. The hydraulic aperture, as calculated from the fracture spacing and permeability (as determined through air-permeability measurements) assuming a cubic law relation, is a closer measure of the smaller apertures in the flow system. Using the hydraulic aperture, a much stronger relationship between permeability and porosity can be developed. This relationship can be approximated as follows:

The initial hydraulic aperture $b_{0,h}$ (m) is calculated using the following cubic law relation:

$$b_{0,h} = [12k_0 s]^{\frac{1}{3}}$$
<div align="right">(F.3)</div>

where k_0 is the initial fracture permeability (m²) and s is the fracture spacing (m). The permeability (k') resulting from a change in the hydraulic aperture, is given by

$$k' = \frac{(b_{0,h} + \Delta b)^3}{12 s}$$
<div align="right">(F.4)</div>

where Δb is the aperture change resulting from mineral precipitation/dissolution.

The aperture change resulting from a calculated volume change can be approximated by assuming precipitation of a uniform layer over the entire geometric surface area of the fracture, assuming also that this area as well as the fracture spacing remains constant. The actual distribution of mineral alteration is much more heterogeneous and depends on many processes that are active at scales much smaller than the resolution of the model; however, the combined effect of the initial heterogeneities and localized precipitation processes can only be treated through model sensitivity studies and experiments.

For a dual permeability model, changes in the fracture porosity are calculated based on the porosity of the fracture medium, so that Δb can be approximated by

$$\Delta b = \frac{\left(\phi'_{fm} - \phi_{fm,0}\right)}{\phi_{fm,0}} b_g$$
<div align="right">(F. 5)</div>

Equations (F.3), (F.4), and (F.5) were implemented in TOUGHREACT with input parameters of b_g and s. An example of this type of porosity and permeability relationship is given in Sample Problem 4 (Section 8.11: Heater Test).

In this example problem, the initial aperture available for precipitation (b_g, the geometric aperture, rather than the hydraulic aperture) was estimated from the ratio of the initial fracture porosity ($\phi_{f,0}$) to the fracture surface area (A_f), as follows:

$$b_g = {\phi_{f,0}}/{A_f}$$

(F.6)

However, the user can, of course, use any methodology to calculate the geometric aperture.

F.3 Matrix Permeability Changes

Option 1: Matrix permeability changes are calculated from changes in porosity using ratios of permeabilities calculated from the Carman-Kozeny relation (Bear, 1972), and ignoring changes in grain size, tortuosity and specific surface area as follows:

$$k = k_i \frac{(1-\phi_i)^2}{(1-\phi)^2}\left(\frac{\phi}{\phi_i}\right)^3$$

(F.7)

Option 2: Modified Hagen-Poiseulle Law. Studies on predicting the permeability of clastic rocks commonly found in sedimentary basins (e.g., sandstones and carbonate rocks) have shown that the permeability can be predicted using a form of the Hagen-Poiseulle equation and knowledge of the pore size distribution, pore throat size, and pore type (Ehrlich et al. 1991). In this study, pore throat sizes and distributions were obtained through a combination of mercury intrusion porosimetry, petrographic image analysis, and image processing.

Option 5: The simple cubic law (Eq. F.2) and the Kozeny-Carman (Eq. F.7) porosity-permeability equations may not reflect the complex relationship of porosity and permeability in geologic media that depends on an interplay of many factors, such as pore size distribution, pore shapes, and connectivity (Verma and Pruess, 1988). Laboratory experiments have shown that modest reductions in porosity from mineral precipitation can cause large reductions in permeability (Vaughan, 1987). Detailed analysis of a large set of field data also indicated a very strong dependence of permeability on small porosity changes (Pape et al., 1999). This is explained by the convergent-divergent nature of natural pore channels, where pore throats can become clogged by precipitation while disconnected void spaces remain in the pore bodies (Verma and Pruess, 1988). The permeability reduction effects depend not only on the overall reduction of porosity, but on the details of the pore space geometry and the distribution of precipitates within the pore space. These may be quite different for different media, which makes it difficult to achieve generally applicable predictions. To evaluate the effects of a more sensitive coupling of permeability to porosity, we also implemented a porosity-permeability relationship presented by Verma and Pruess (1988):

$$\frac{k}{k_i} = \left(\frac{\phi - \phi_c}{\phi_i - \phi_c}\right)^n$$

<div align="right">(F.8)</div>

where ϕ_c is the value of "critical" porosity at which permeability goes to zero, and n is a power law exponent. Parameters ϕ_c and n are medium-dependent. An example of this porosity-permeability relationship is given in Sample problem 8 (Section 8.8: Injection well scaling).

F.4   Effects of Permeability and Porosity Changes on Capillary Pressures

Permeability and porosity changes will likely result in modifications to the unsaturated flow properties of the rock. For cylindrical pore throats changes to unsaturated flow properties are approximated by modification of the calculated capillary pressure (*Pc*) using the Leverett scaling relation (Slider, 1976) to obtain a scaled *Pc´* as follows:

$$Pc' = Pc\sqrt{\frac{k_i\phi}{k\phi_i}}$$

<div align="right">(F.9)</div>

For fractures, the capillary pressures are scaled assuming channel flow,

$$Pc' = Pc\left(\frac{k_i\phi}{k\phi_i}\right)^{1/3}$$

<div align="right">(F.10)</div>

Since many problems may involves fractures and rock matrix (e.g., dual-permeability), a third option allows for a linear porosity-dependent scaling between capillaries and channels (fractures)

Scaled capillary pressures are subject to the maximum capillary pressure prescribed in the capillary pressure function in the ROCKS or RPCAP blocks (see TOUGH2 V.2 users manual).

Appendix G Mineral Reactive Surface Areas

This appendix describes how input values of surface areas are used to calculate the reactive surface area needed for kinetic rate laws (e.g., in equations B.6 and B.9). The general methodology implemented into TOUGHREACT is presented first (Section G.1), followed by suggestions on how to calculate and input surface areas for fractures (Section G.2) and a porous rock matrix (Section G.3). Surface areas are input as variable AMIN on record Imin-6.1 (in file chemical.inp), using a choice of units defined by flag IMFLG on the same input record. Note that any approach may be used to calculate input surface areas as long as the correct units are entered for the specified value of IMFLG.

G.1   General Methodology

The following general relationship is implemented into TOUGHREACT to compute reactive surface areas of minerals:

$$A_r = (V_{frac} A_m + A_{prc}) / C_w \qquad \text{(G.1)}$$

with:

A_r Effective reactive surface area of minerals in units of $m^2_{mineral}/kg_{water}$ for input into kinetic rate laws (e.g. equations B.6 and B.9)

Am   Surface area of minerals in units of $m^2_{mineral}/m^3_{mineral}$

Aprc   Precursor surface area (optional) in units of $m^2_{surface}/m^3_{medium}$

Vfrac   Mineral volume fraction in units of $m^3_{mineral}/m^3_{medium}$

Cw   Wetted-surface conversion factor in units of kg_{water}/m^3_{medium}

The values of A_m, V_{frac}, and C_w change in the course of a simulation as minerals dissolve and precipitate, and as the liquid saturation of the medium fluctuate. A_m is computed, in part, from input surface areas. A_{prc}, however, is an input parameter that remains constant in the course of a simulation. Various approaches are followed to compute A_m, V_{frac}, and C_w from input parameters and/or model assumptions, depending on whether a mineral is present or not, which type of surface area model is selected, which type of medium is considered (fractures or matrix), and which units are chosen to input surface areas. Approaches followed to compute these variables are described below.

Mineral volume fraction V_{frac}. For all minerals (initially present or not) included in a simulation, a minimum value of V_{frac} is calculated as

$$V^0_{frac} = maximum (\text{RNUCL}(1-\phi_{med}); 10^{-10}) \qquad \text{(G.2)}$$

where RNUCL in an assumed minimum volume fraction (in $m^3_{mineral}/m^3_{solids}$) (entered on record Miner-2.2 in file chemical.inp) and ϕ_{med} is the porosity of the medium. When a mineral is not initially present (i.e., case of a secondary phase that forms during a simulation), V_{frac} in Equation (G.1) always takes the value of V^0_{frac}. For minerals that are present in the modeled system, V_{frac} is initially computed from input mineral volume fractions f_m (in $m^3_{mineral}/m^3_{solids}$) (VOL on record Imin-6 in file chemical.inp) and porosity of the medium (ϕ_{med}, read in flow.inp or INCON files) as:

$$V_{frac} = f_m (1-\phi_{med}) \qquad \text{(G.3)}$$

The values of V_{frac} are then continuously updated from the computed amounts of minerals, as these dissolve and/or precipitate. Note that if, at any time, V_{frac} is less than V^0_{frac}, the value of V^0_{frac} is used instead of V_{frac} in equation (G.1).

Surface area A_m. Values of A_m are calculated as

$$A_m = A^0{}_m + A_{nucl}$$

(G.4)

$A^0{}_m$ is the input mineral surface area (AMIN, if IMFLG≠3, on record Imin-6.1 in chemical.inp). It is always internally converted to units of $m^2_{mineral}/m^3_{mineral}$. A_{nucl} is a surface area used to approximate nucleation effects (this is not a nucleation model!) By default, A_{nucl} is always set to zero if the value of RAD (on record Imin-6.1 in file chemical.inp) is set to zero. If RAD ≠0, a simple model is implemented to compute A_{nucl} as a function of mineral grain size, with RAD entered as the initial grain radius (in m). This is done by assuming simple cubic packing of spherical grains of radius r. This cubic arrangement of spheres yields, in a cube of side $4r$ and volume $(4r)^3$, a total of 8 spheres, each of radius r, volume $4/3\ \pi r^3$, and area $4\pi r^2$. Thus the surface area A_{nucl} (as the area of the spheres divided by the volume of the cube) is computed as

$$A_{nucl} = 0.5/r$$

(G.5)

For minerals not initially present, r is initially taken as the value of RAD (in m). Only on precipitation, the value of r is increased as the mineral forms, such that A_{nucl} decreases with increasing mineral amounts. This is accomplished by tying the increase of V_{frac} to r through a variable, n_{grain}, expressing the number of mineral grains per volume medium as follows

$$n_{grain} = 0.125\ V_{frac}\ /\ r^3$$

(G.6)

Equation (G.6) is also derived assuming simple cubic packing of spherical grains. For minerals not initially present, the number of mineral grains is initially calculated using Equation (G.6) with $V_{frac} = V^0{}_{frac}$ and r = RAD. At subsequent time steps, as V_{frac} increases with mineral precipitation, n_{grain} is decreased proportionally to $V_{frac}/\ V^0{}_{frac}$ (an assumption) and the grain radius is recomputed by re-expressing Equation (G.6) to yield values of r:

$$r = \sqrt[3]{\frac{0.125 V_{frac}}{n_{grain}}}$$

(G.7)

As r grows and n_{grain} diminishes, A_{nucl} decreases to a point when $A_{nucl} << A^0{}_m$ and $A_m \approx A^0{}_m$ in Equations (G.4) and (G.1). On precipitation, because n_{grain} is forced to decrease, A_r also decreases as r grows, as long as $A_{nucl} > A^0{}_m$. In contrast, on dissolution, n_{grain} is kept constant (i.e., not recomputed), such that if $A_{nucl} > A^0{}_m$, A_r always keeps decreasing with decreasing r (as seen by substituting Equations G.3, G.4, and G.5 into Equation G.1).

Wetted-surface conversion factor C_w. This conversion factor (in units of kg_{water}/m^3_{medium}) usually takes the form

$$C_w = \rho_w \phi_{med}\ S_w$$

(G.8)

where ρ_w is the water density (kg/L), ϕ_{med} is the porosity of the medium, and S_w is liquid saturation. For a fully saturated system, $S_w = 1$. For an unsaturated system, $S_w < 1$. However, as S_w goes to zero, C_w goes to zero, and therefore the wetted reactive surface area A_r, which is proportional to $1/C_w$ (Equation G.1), tends to infinity. Clearly, at a very low liquid saturation, the surface area of the rock contacted by water is likely much smaller than the total area. Two methods are implemented to address this problem. The first method assumes that the wetted surface area diminishes proportionately to the liquid saturation. This behavior is achieved by multiplying the right side of Equation (G.1) by S_w. This cancels out S_w in Equation (G.8), such that the quantity C_w in Equation (G.1) becomes, in effect

$$C_w = \rho_w \phi_{med} \tag{G.9}$$

This method is implemented for both porous media and fractured systems. However, an other method is applied for fractured systems if the active-fracture model is enabled (which is done by specifying non-zero active-fracture parameters (CP(6), in the third record of the ROCKS block in file flowinp). This method employs the active-fracture-model of Liu et al. (1998) modified to consider water-rock reactions taking place below the residual saturation in fractures. The form of the active fracture parameter for reaction is given by the following set of equations:

$$S_{ar} = (S_w - S_m)/(1 - S_m) \tag{G.10}$$

$$a_{fmr} = S_{ar}^{(1+\gamma)} \tag{G.11}$$

where S_m is the minimum liquid saturation for which water-rock reactions are considered (input parameter SL1MIN on Record-3 in file solute.inp), S_{ar} is an effective saturation for reaction, and γ is the active fracture parameter. The factor that reduces the surface area contacted by water is given by a_{fmr}. Generally, S_m is set to a small value (e.g., 1×10^{-4}), to ensure that reactions take place until virtually no water is left (e.g., during dryout via ventilation or heating). Using this model, the quantity C_w is computed as

$$C_w = \rho_w \phi_{med} S_w / a_{fmr} \tag{G.12}$$

G.2 Estimation of Surface Areas for Fractures

In the dual permeability method, the porosity of the fracture medium could be taken as 1.0. However, for modeling of mineral dissolution and precipitation, there would then be no rock to dissolve. Therefore, a non-zero fracture-medium porosity (ϕ_{med}) must always be assumed for input into simulation (typically $0.5 < \phi_{med} < 0.9$; this porosity is not to be confused with the true fracture porosity ϕ_f). If the dissolution rates of minerals are small (which is the case for many minerals at temperatures below 100°C), only a small volume of rock adjoining the open space of the fracture needs to be considered as the starting rock fraction (i.e., ϕ_{med} can be large, as long as < 1).

Reactive surface areas of minerals on fracture walls can be calculated from the fracture-matrix interface area/volume ratio, the fracture porosity, and the derived mineral volume fractions. These areas can be calculated based on the fracture densities, fracture porosities, and mean fracture diameter. The wall of the fracture can be treated as a surface covered by mineral grains having the form of uniform hemispheres. The grain diameter and spatial density are not considered in this method, so that the area is actually only marginally greater than the fracture geometric surface area. Using this approach, the geometric surface area of the fracture wall can be approximated by:

$$A = \frac{\pi A_{f\text{-}m}}{2\phi_f}$$
(G.13)

where A is the "reactive" surface area (in units of $m^2_{reactive\ surface}/m^3_{fracture\ medium}$), $A_{f\text{-}m}$ is the fracture-matrix interface area/volume ratio (in units of $m^2_{reactive\ surface}/m^3_{total\ fracture+matrix\ medium}$), and ϕ_f is the true fracture porosity of the rock. The factor of $\pi/2$ is a roughness factor equal to the actual surface area of solid grains on the fracture plane, divided by the fracture plane surface, given by cubic packing of spherical grains.

Surface areas calculated using Equation (G.13) are input as AMIN with IMFLG=3 on record Imin-6.1 in file chemical.inp. In this case, input AMIN values correspond to A_{prc} in Equation (G.1), and values of A^0_m in Equation (G.4) are internally set to zero (therefore $A_m = A_{nucl}$ in Equation G.1). In this scenario, A in Equation G.13 is assumed to be the same for all minerals.

An alternative is to consider mineral proportions in the surface coverage of fractures. Assuming that the fracture coverage for each mineral is proportional to the mineral volume fraction, V_{frac}, the surface area for each mineral, A' (in units of $m^2_{mineral}/m^3_{fracture\ medium}$) can be calculated as

$$A' = A\ V_{frac}$$
(G.13)

Values of A' calculated in this way are input as AMIN with IMFLG=2 on record Imin-6.1 in file chemical.inp. For minerals not initially present, V_{frac} in Equation (G.13) must be taken as V^0_{frac} (Equation G.2) for internal consistency. In this case, the input AMIN values correspond to A^0_m in Equation (G.1), and A_{prc} is this equation is internally set to zero.

G.3   Estimation of Surface Areas in the Rock Matrix (Porous Medium)

One method to calculate the reactive surface areas of minerals in a rock or granular material is to use a geometric area of a cubic array of truncated spheres to make up the framework of the rock (Sonnenthal and Ortoleva, 1994). Clay minerals can be considered as coatings of plate-like grains. The mineral surface areas of framework grains (truncated spheres) in contact with the open pore space can be calculated using an initial grain diameter, followed by successive truncation of the grains in the vertical direction until the porosity of this system is close to the measured porosity of the rock. The abundance of secondary phases (i.e., those that

formed as alteration products or low-temperature coatings on the primary assemblage), such as clay minerals, can be used to reduce the free surface area of the framework grains. The surface areas of the secondary phases can be calculated based on their size and morphology.

A more approximate but very simple method is to consider geometric surface areas for either single sphere, simple cubic packing of untruncated spheres, or cubic-centered packing of untruncated spheres. The surface area is obtained by dividing the area of the spheres by the volume of the spheres (for the various packing arrangements) as shown below.

Single sphere – area $4\pi r^2$, volume $4/3\ \pi r^3$:

$$A = 3/r \tag{G.14}$$

Simple cubic packing – 8 spheres of total area $8 \times 4\pi r^2$, in a cube of volume $(4r)^3$:

$$A = 0.5/r \tag{G.15}$$

Cubic-close packing – 4 spheres of total area $4 \times 4\pi r^2$, in a cube of volume $(2\sqrt{2}\ r)^3$:

$$A = \pi / (\sqrt{2}\ r) \quad = 2.22/r \tag{G.16}$$

Note that differences in the constant terms in these equations are much smaller than the typical order-of-magnitude uncertainty of surface areas. If the grain radius r is in units of m, values of A calculated in this way are in units of $m^2_{mineral}/m^3_{mineral}$ and can be input directly as AMIN with flag IMFLG=1 in record Imin-6.1 (in file chemical.inp). Surface areas in units of cm^2/g can be calculated from

$$A' = 100\ A\ /\ \rho_m = 100\ A\ M_m\ /\ V_m \tag{G.17}$$

where ρ_m, M_m and V_m are the mineral density in g/cm^3, molecular weight in mol/g, and molar volume in cm^3/mol (M_m and V_m can be taken from record Mineral-1 in the thermodynamic database). In this case, A' is entered (in file chemical.inp) as AMIN with flag IMFLG=0 on record Imin-6.1.

Appendix H Calculation of Activity and Fugacity Coefficients

H.1   Extended Debye-Hückel Model for Ionic Species and Water

Activity coefficients of charged aqueous species and the water activity are computed using the extended Debye-Hückel model presented by Helgeson et al. (1981), often refered to as the HKF model (for Helgeson, Kirkham, and Flowers). We will use this accronym, below, to refer to the model, its authors, or their published paper.

The HKF model is applied making the assumption that the dominant cation and anion in solution are sodium and chloride, respectively, which entails limits on the model applicability. In addition, the Debye-Hückel model, even if extended, technically only applies to dilute solutions. For this reason, for applications at elevated ionic strengths (> ~1 molal), the model should be very carefully applied, with full knowledge its limitations, as discussed further below. Note that at ionic strength < ~1 molal, the HKF model yields results very close to the more commonly used "b-dot" extended Debye-Hückel model (Helgeson, 1969). Details on the formulation of activity coefficients for charged species, water activity, and the HKF model applicability are presented below in Sections H.1.1, H.1.2, and H.1.3, respectively.

H.1.1 Activity Coefficients of Charged Aqueous Species

The assumption is made that the dominant cation and anion in solution are sodium and chloride, respectively, so that HKF Equation (298) can be used directly, as follows:

$$\log (\gamma_j) = -\frac{A_\gamma \, z_j^2 \, I^{0.5}}{\Lambda} + \log (1 + 0.0180153 m^*) - \left[\omega_j b_{NaCl} + b_{Na^+,Cl^-} - 0.19(|z_j|-1) \right] I \tag{H.1}$$

and

$$\Lambda = 1 + \mathring{a} \, B_\gamma \, \bar{I}^{1/2} \tag{H.2}$$

$$\omega_j = \eta \frac{z_j^2}{r_{e,j}} \tag{H.3}$$

where the subscript j refers to each ion, γ is the activity coefficient of the ion, Debye-Huckel parameters b_{Na^+,Cl^-}, b_{NaCl}, $A\gamma$ and $B\gamma$ are given in HKF Tables 1, 29, and 30, Debye-Huckel parameter $\mathring{a}$ is calculated as discussed below, z is the ion electric charge, I is taken as the true ionic strength of the solution, ω is the Born coefficient, η is a constant equal to 1.66027 (Å cal/mol), and $r_{e,j}$ is the effective ionic radius given in HKF Table 3 or estimated as shown on Table H.1-1 when not available.

Debye-Huckel parameters b_{Na^+,Cl^-}, b_{NaCl}, $A\gamma$ and $B\gamma$ were regressed as a function of temperature and the resulting functions and regression coefficients are currently built into TOUGHREACT. Values of $\mathring{a}$ are calculated by TOUGHREACT using effective ionic radii $r_{e,j}$. Making the assumption that NaCl is the dominant electrolyte, and using the ion charge to determine stoichiometry coefficients, HKF Equation (125) simplifies to (as implemented in models by Reed, 1982):

$$\mathring{a}_j = 2 \, (r_{e,j} + 1.91 \, |z_j|) \, / \, (|z_j| + 1) \;\; \text{for anions} \tag{H.4}$$

$$\mathring{a}_j = 2\,(r_{e,j} + 1.81\,|z_j|)\,/\,(|z_j| + 1)\ \text{ for cations} \tag{H.5}$$

where the subscript j refers to each ion and other parameters are as defined above. The values of 1.91 and 1.81 in the above equations correspond to r_{e,Na^+} and r_{e,Cl^-}, respectively. Values of $r_{e,j}$ are input from the TOUGHREACT database and can be changed as deemed necessary in this database.

Table H.1—1   **Estimated values of effective ionic radii ($r_{e,j}$) currently in the TOUGHREACT thermodynamic database for species that are not reported in HKF Table 3. When available, values from HKF Table 3 are used directly instead of those shown here.**

Ion Charge	$r_{e,j}$	Source
-1	1.81	Cl- value
-2	3.00	Rounded average of CO3-- and SO4-- values
-3	4.2	Estimated from straight line fit with charge
+1	2.31	NH4+ value
+2	2.8	Rounded average for +2 species in HKF Table 3
+3	3.6	Rounded average for +3 species in HKF Table 3
+4	4.5	Estimated using HKF Equation 142 and average crystallographic radii of +4 species in CRC Handbook
< -3		Linear Extrapolation (charge × 4.2/3.0)
> +3		Linear Extrapolation (charge × 4.5/4.0)

H.1.2 Activity of Water

First, a simplification of HKF Equation (190) is used to compute the osmotic coefficient of the solution, Φ, as follows:

$$\Phi = -\frac{2.303}{m^*}\sum_j\left[m_{t,j}\left[\frac{A_\gamma\,z_j^2\,\bar{I}^{0.5}\,\sigma}{3} + \frac{\log\,(1+0.0180153m^*)}{0.0180153\,m^*} - \right. \right.$$
$$\left.\left. - 0.5\,(\omega_j b_{NaCl}\,\bar{I}) + (b_{Na^+,Cl^-} - 0.19(|z_j|-1))\frac{mchr}{2}\right]\right] \tag{H.6}$$

with

$$\sigma = \frac{3}{\mathring{a}\,B_\gamma^3\bar{I}^{3/2}}\left[\Lambda - \frac{1}{\Lambda} - 2\ln(\Lambda)\right]$$

and with

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$$\Lambda = 1 + \mathring{a} \, B_\gamma \, \bar{I}^{1/2} \qquad \text{and} \qquad \omega_j = \eta \, \frac{z_j^2}{r_{e,j}}$$

where the subscript *j* refers to each charged species in solution, m* is taken as the sum of the molalities of all species in solution, m_t is the total molality of each charged species, *mchr* is the sum of the molalities of all charged species, and $\bar{I}$ is taken as the stoichiometric ionic strength. Other parameters are as defined for Equation (H.1). The simplifications made in Equation (H.6) assume dominance of NaCl in solution, and are essentially the same as the simplifications made to derive Equation (H.1). Two differences are the use of the stoichiometric ionic strength instead of the true ionic strength, and the use of *mchr*/2 instead of true ionic strength. These modifications were made because they seemed to reproduce water activity data reported by Robinson and Stokes (1965) better than without these modifications. Once the osmotic coefficient is calculated, the water activity is then given by the HKF Equation (126), as:

$$\ln(a_w) = -\Phi \, m* \, \frac{1}{55.51}$$

(H.7)

H.1.3 Applicability of the HKF Extended Debye-Hückel Model

It is recommended that users understand the HKF model and its limitations before applying it at ionic strengths greater than about ~1 molal. The limits of applicability of this model depend, in part, on how well the assumption of NaCl-dominance in solution is satisfied. Also, consistency between the activity coefficient model and the types of ion pairs included in the thermodynamic database is critical. Good examples are the $NaCl^0$ and $CaCl_2^0$ (and $CaCl^+$) ion pairs. HKF fitted their Debye-Hückel parameters assuming that no significant formation of these ion pairs took place (i.e., the effect of these ion pairs are implicitly taken into account in the model parameters). Therefore, for applications at elevated ionic strengths (> ~1 molal), good results are obtained only after removing these ion pairs from the thermodynamic database.

With careful testing for each particular system, including determination of which ion pairs to include (or not) into the thermodynamic database, this model can be applied to ionic strengths up to about 2 molal, and possibly to up to 4 molal for simple salt systems. However, no general rule can be made as to the limits of applicability, except that we do not recommend using this model at ionic strengths greater than ~4 molal, especially at higher temperatures. It should be noted that for salt mixtures, the model limit should be evaluated by the user on a case-by-case basis, taking into consideration the overall reactive transport model uncertainty and the goals of the modeling work. As a general guideline, an ionic strength limit of 2 molal may be appropriate for many applications, and values greater than 4 molal should not be considered.

To evaluate the range of model applicability for single salt systems, speciation calculations (one grid block, no transport) were run for solutions of various single salts. Results were then compared with

published experimental data (Robinson and Stokes 1965; Colin et al. 1985; and Ananthaswamy and Atkinson, 1985). Only electrolyte activity can be measured, from which mean activity coefficients can be derived (individual activity coefficients cannot be measured). For this reason, individual activity coefficients activities calculated with the HKF model need to be converted for comparisons to measured data (or vice versa). For an electrolyte k (e.g., NaCl) consisting of ionic species j (e.g., Na$^+$ and Cl$^-$), the mean activity coefficient, $\gamma_{k\pm}$, and electrolyte activity, a_k, can be related to the activity coefficients γ_j and activities a_j of individual ionic species using the following relationships (e.g., Robinson and Stokes, 1965, Equations 2.12, 2.8, and 2.13, respectively):

$$\gamma_{k\pm} = \left(\prod_j \gamma_j^{\upsilon_{j,k}} \right)^{1/\upsilon_k}$$

(H.8)

$$a_k = \prod_j (a_j)^{\upsilon_{j,k}}$$

(H.9)

$$a_k = \prod_j (\upsilon_{j,k}^{\upsilon_{j,k}})(m_k \gamma_{k\pm})^{\sum_j \upsilon_{i,k}}$$

(H.10)

where $\upsilon_{j,k}$ are stoichiometric coefficients of ionic species j in electrolyte k, and m_k is the electrolyte molality. For comparison with literature data, computed activity coefficients for individual ions (output in file *chdump.out*) were converted to mean activity coefficients using Equation (H.8). Activities for individual ions were also calculated from individual molalities (m_j) and activity coefficients (γ_j) (using the relationship $a_j = \gamma_j m_j$), then converted to mean activities using Equation (H.9). As necessary, Equation (H.10) was also used to convert mean activity coefficients from the literature data to mean activities. Finally, osmotic coefficients (Φ) from the literature were converted to water activities (a_{H2O}) using Equation (H.7). After these conversions, computed and measured data could be compared, with results summarized in Figures H.1-1 through H.1-5, and in Table H.1-2. As noted above, computations without including the secondary species NaCl$_{(aq)}$, CaCl$^+$, and CaCl$_{2(aq)}$ in the thermodynamic database provide best results, because the HKF model was developed assuming no explicit ion association for these salts. At elevated ionic strengths (> 1 molal), the model reproduces fairly well the mean activity coefficients of NaCl solutions up to at least 6M NaCl (ionic strength 6) (Figures H.1-1, H.1-3, and H.1-4). The reverse is true for species like MgSO$_4$ and Na$_2$SO$_4$, for which accurate activities cannot be computed without including the MgSO$_4$ and NaSO$_4^-$ species in the thermodynamic database, because the significant association of Mg and Na with SO$_4$ was considered in the HKF model. In this case, using dissociation constants from Shock et al. (1989) for these species, mean activities determined by Robinson and Stokes (1965) at 25°C can be reproduced fairly well up to 2M MgSO$_4$ (ionic strength = 8) and 1M Na$_2$SO$_4$ (ionic strength = 3) (Figure H.1-2). Activity coefficients and activities in CaCl$_2$ solutions are also reasonably reproduced up to about 1.5 m CaCl$_2$ (ionic strength = 4.5 molal) (Figures H.1-1, H.1-3, and H.1-5).

Figure H.1—2   Activities of MgSO$_4$ and Na$_2$SO$_4$ at 25°C derived from individual activity coefficients calculated with Equation (H.1). Symbols represent data from measurements by Robinson and Stokes (1965). Actual activities, rather than activity coefficients, are compared here because significant ion association takes place.
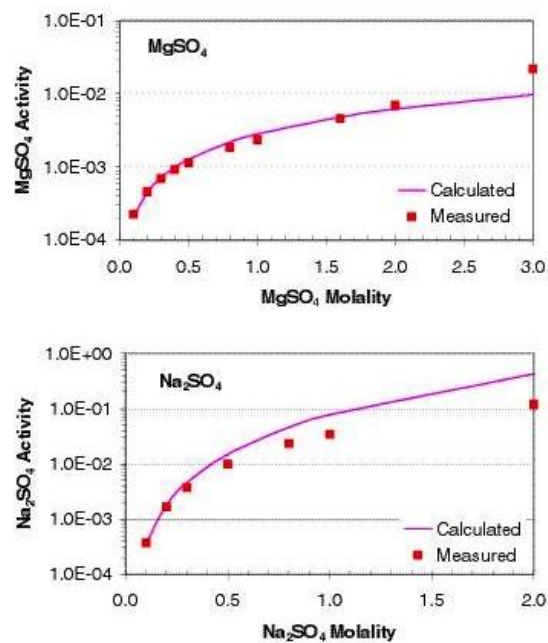
Figure H.1—3   Activities of water in NaCl and CaCl₂ solutions at 25°C calculated with Equations (H.6) and (H.7). Symbols represent data from measurements by Robinson and Stokes (1965).
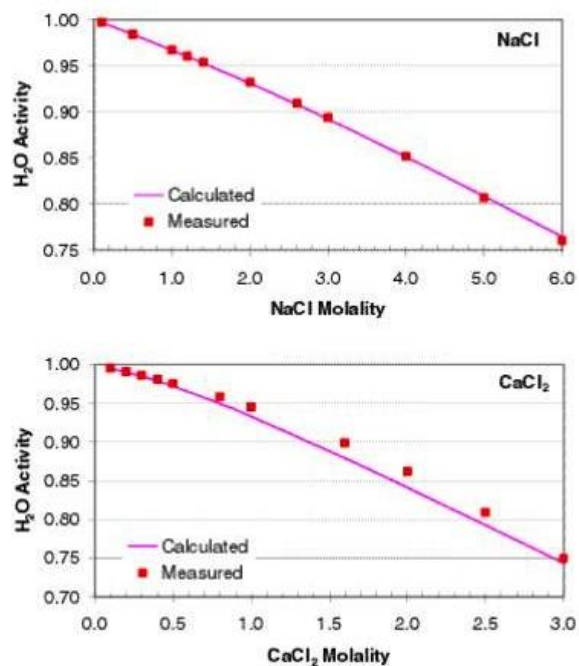
Figure H.1—4 **Comparison of measured (Colin et al. 1985) and computed activities for NaCl solutions. Note that the NaCl$_{(aq)}$ species is excluded from the simulation for consistency with the activity coefficient model.**
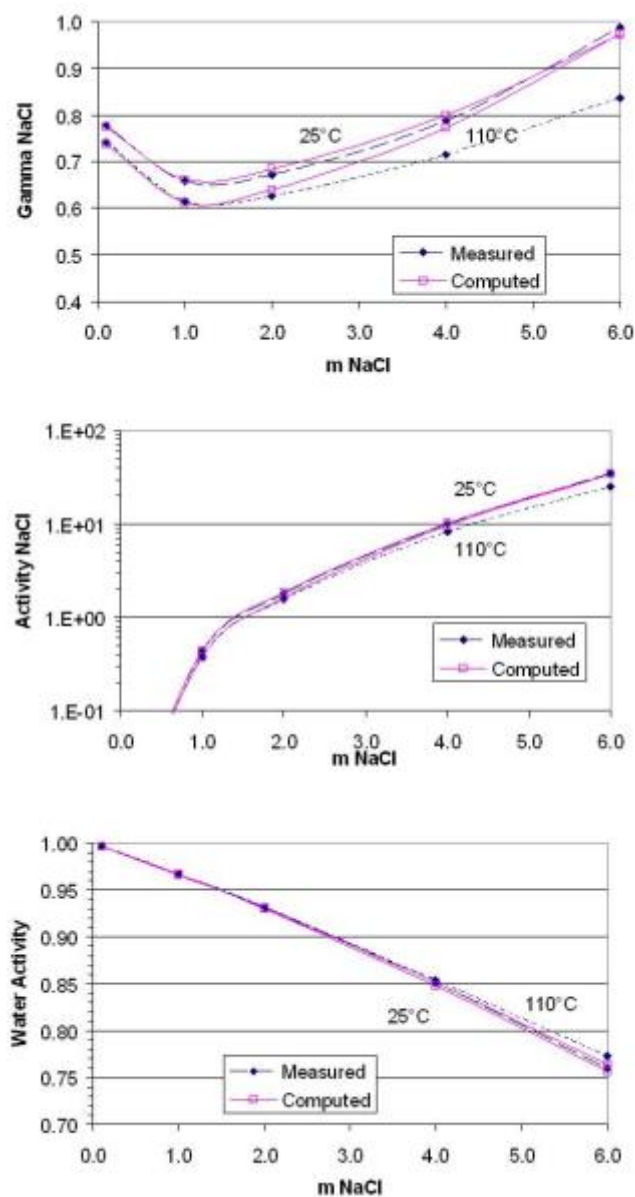
Figure H.1—5 Comparison of measured (Ananthaswamy and Atkinson, 1985) and computed activities for CaCl$_2$ solutions. Note that the CaCl$_{2(aq)}$ and CaCl$^+$ species are excluded from the simulation for consistency with the activity coefficient model.

Temp (°C)	m NaCl	Ionic Str.	γ_{NaCl}± Meas[1]	γ_{NaCl}± Comp	% Diff	a_{NaCl} Measured[1]	a_{NaCl} Computed	% Diff	a_{H2O} Meas[1]	a_{H2O} Comp	% Diff
			Mean activity coefficient			Mean activity			Water activity		
25	0.1	0.1	0.7753	0.775	-0.4	6.05E-03	6.00E-03	-0.7	0.9966	0.9967	0.0
25	1	1	0.65805	0.661	0.5	4.33E-01	4.37E-01	0.9	0.9668	0.9667	0.0
25	2	2	0.67131	0.684	1.8	1.80E+00	1.87E+00	3.7	0.934	0.930	-0.1
25	4	4	0.78809	0.800	1.5	9.94E+00	1.02E+01	2.9	0.8512	0.851	0.0
25	6	6	0.98882	0.972	-1.7	3.52E+01	3.40E+01	-3.3	0.7601	0.764	0.5
110	0.1	0.1	0.74109	0.736	-0.7	5.49E-03	5.41E-03	-1.4	0.9967	0.9967	0.0
110	1	1	0.61371	0.612	-0.2	3.77E-01	3.75E-01	-0.4	0.9670	0.9667	0.0
110	2	2	0.62566	0.639	2.1	1.57E+00	1.63E+00	4.3	0.9317	0.930	-0.1
110	4	4	0.71514	0.772	7.9	8.18E+00	9.53E+00	17	0.8542	0.848	-0.8
110	6	6	0.83637	0.974	17	2.52E+01	3.42E+01	36	0.7727	0.756	-2.1

Temp (°C)	m CaCl2	Ionic Str.	γ_{CaCl2}± Measured[2]	γ_{CaCl2}± Computed	% Diff	a_{CaCl2} Measured[2]	a_{CaCl2} Computed	% Diff	a_{H2O} Measured[2]	a_{H2O} Computed	% Diff
			Mean activity coefficient			Mean activity			Water activity		
25	0.001	0.003	0.8881	0.888	0.0	2.80E-09	2.80E-09	0.0	0.9999	1.00	0.0
25	0.1	0.3	0.5164	0.507	-1.8	5.51E-04	5.21E-04	-5.4	0.9954	0.9955	0.0
25	0.5	1.5	0.4453	0.450	1.2	4.41E-02	4.57E-02	3.5	0.9756	0.9751	-0.4
25	1	3	0.4959	0.522	5.3	4.88E-01	5.69E-01	17	0.9451	0.9219	-1.7
25	1.6	4.8	0.6367	0.675	6.1	4.23E+00	5.04E+00	19	0.8989	0.8663	-4.0
100	0.001	0.003	0.8695	0.869	-0.1	2.63E-09	2.62E-09	-0.2	0.9999	1.00	0.0
100	0.1	0.3	0.4530	0.438	-3.4	3.72E-04	3.35E-04	-9.9	0.9956	0.9956	0.0
100	0.5	1.5	0.3568	0.334	-6.3	2.27E-02	1.87E-02	-18	0.9770	0.9766	-0.1
100	1	3	0.3703	0.334	-9.7	2.03E-01	1.50E-01	-26	0.9493	0.9446	-0.4
100	1.6	4.8	0.4381	0.366	-16	1.38E+00	8.04E-01	-42	0.9079	0.9082	-0.7

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Table H.1—2   **Comparison of measured and computed activity data for NaCl and CaCl₂ solutions. Note that the NaCl$_{(aq)}$, CaCl⁺, and CaCl$_{2(aq)}$ secondary species are excluded from the simulation for consistency with the activity coefficient model.**

[1]Data from, Colin et al., 1985; [2]Data from Ananthaswamy and Atkinson, 1985

Activity Coefficients of Neutral Aqueous Species

For dissolved gases with the following exact names in the thermodynamic database, activity coefficients are computed using an equation derived from correlations developed by Drummond (1981) for CO_2 gas dissolution in NaCl solutions up to 6 molal (see also Section B.4 in Appendix B):

'co2(aq)' or 'CO2(aq)'

'ch4(aq)' or 'CH4(aq)'

'h2(aq)' or 'H2(aq)'

'h2s(aq)' or 'H2S(aq)'

'o2(aq)' or 'O2(aq)'

'so2(aq)' or 'SO2(aq)'

$$\ln(\gamma) = (C + F\,T + G/T)\,I - (E + H\,T)\,I/(I + 1)$$

(H.11)

where I and T are is the true ionic strength and absolute temperature, respectively, and C, E, F, G, and H are fit coefficients as follows:

C	-1.0312
E	0.4445
F	0.0012806
G	255.9
H	-0.001606

For other uncharged molecular species activity coefficients are set to one by default or can be optionally computed as (e.g. Langmuir 1997):

$$\log(\gamma_i) = K_i\,I$$

(H.12)

where K_i are salting-out coefficients and I is the true ionic strength of the solution. Currently, values of K_i are assumed to be independent of temperature. These salting-out coefficients are input from the TOUGHREACT thermodynamic database (A0 in the primary and secondary species blocks, see Section 6.4), and default to zero (unit activity coefficients).

H.1.4 Fugacity Coefficients of Gases

When TOUGHREACT is compiled with the TOUGH2 module ECO2N, the fugacity coefficients of CO_2 are computed within the ECO2N module as a function of pressure, temperature, and composition, using the H_2O-CO_2 mutual solubility model of Spycher et al. (2005) for pure water and saline solutions (for temperature and pressure ranges of 10–110°C and 1–600 bar).

When TOUGHREACT is compiled with other EOS modules, or for initial speciation calculations, fugacity coefficients of CO_2, H_2, and CH_4, are computed as a function of pressure and temperature only (ideal mixing of real gases) using the correlations of Spycher and Reed (1988) (for temperature and pressure ranges of ~50–300°C and 1–500 bar for CO_2; 0–1000°C and 1–3000 bar for H_2; and 25–300°C and 1–500 bar for CH_4). Fugacity coefficients of other gases (besides H_2O gas) are assumed equal to 1 (ideal gas behavior and ideal mixing). The calculation of fugacity coefficients can be turned on or off for various EOS modules (except ECO2N) by setting flag iFugaC to 0 (off) or 1 (on) in subroutine Gas_Fuga_Coe (in treact_v2.f).

The behavior of H_2O gas (ideal or non-ideal), and computation of H_2O gas fugacity, is always taken into account by the selected TOUGH2 EOS module compiled with TOUGHREACT.

Appendix I   Treatment for Mineral Solid Solutions

Currently, the only solid solution model implemented in TOUGHREACT is an ideal solid solution model. This model is only available for minerals that react under kinetic constraints.

The condition of equilibrium for a solid solution is

$$\left(Q_{ss} \Big/ K_{ss} a_{ss} \right) = 1$$

(I.1)

where the subscript *ss* refers to the solid solution, and Q and K are the ion activity product and equilibrium constant for that solid solution, respectively, and a is the activity of the solid solution. By convention, $a_{ss} = 1$.

A similar expression can be written for the condition of equilibrium for each end-member of the solid solution:

$$\left(Q_i \middle/ K_i a_i \right) = 1 \tag{I.2}$$

In this case, the subscript i refers to each end member, and $a_i \neq 1$.

In the case of an ideal solid solution, the activity of each endmember, ai, is assumed to equal its mole fraction xi in the solid solution. Making this assumption and combining Equations (I.1) and (I.2) (with ass = 1) yields:

$$\left(Q_i \middle/ K_i x_i \right) = \left(Q_{ss} \middle/ K_{ss} \right) \tag{I.3}$$

For a solid solution composed of n end-members, Equation (I.3) is consistent with the relation (e.g. Reed, 1982):

$$\left(Q_{ss} \middle/ K_{ss} \right) = \sum_{i=1}^{n} \left(Q_i \middle/ K_i \right) \tag{I.4}$$

Alternatively, combining Equations (I.3) and (I.4) yields, at equilibrium

$$x_i = \frac{\left(Q_i \middle/ K_i \right)}{\sum_{i=1}^{n} \left(Q_i \middle/ K_i \right)} \tag{I.5}$$

For a solid solution reacting under kinetic constraints we can then write a rate law similar to Equation (B.5) in Appendix B.

$$R_{ss} = k_{ss} A_{ss} \left[1 - \left(Q_{ss} \middle/ K_{ss} \right) \right] \tag{I.6}$$

where R, A, and k stand for the reaction rate, surface area, and rate constant of the whole solid solution ss. To treat the solid solution as a function of only individual endmembers, i, we write:

$$R_{ss} = \sum_{i=1}^{n} \left(x_i R_i \right) \tag{I.7}$$

with x_i and R_i being the mole fraction and rate, respectively, for each endmember of the solid solution. The rate of each endmember can be expressed as

$$R_i = k_i A_{ss} \left[1 - \left(\frac{Q_i}{K_i a_i} \right) \right]$$

<div align="right">(I.8)</div>

where k_i is the rate constant of each endmember. Assuming ideal behavior ($a_i = x_i$) and substituting Equation (I.8) into Equation (I.7) we get:

$$R_{ss} = \sum_{i=1}^{n} (x_i R_i) = \sum_{i=1}^{n} \left(x_i k_i A_{ss} \left[1 - \left(\frac{Q_i}{K_i x_i} \right) \right] \right)$$

<div align="right">(I.9)</div>

which can be further expanded as

$$R_{ss} = \sum_{i=1}^{n} \left(k_i A_{ss} \left[x_i - \left(\frac{Q_i}{K_i} \right) + 1 - 1 \right] \right) = \sum_{i=1}^{n} \left(k_i A_{ss} \left[1 - \left(\frac{Q_i}{K_i} \right) \right] + k_i A_{ss} [x_i - 1] \right)$$

<div align="right">(I.10)</div>

Equation (I.10) leads to the final relationship

$$R_{ss} = \sum_{i=1}^{n} \left[R_i' + k_i A_{ss} (x_i - 1) \right]$$

<div align="right">(I.11)</div>

where R_i' is the rate of the endmember as a pure mineral (that is, with $a_i = 1$ in Equation (I.8)).

This approach is implemented in TOUGHREACT by adding a term equal to $k_i A_{ss} (x_i - 1)$ to the rates R_i' computed for each individual mineral that is part of a solid solution. In doing so, Equation (I.11) is implicitly treated by the total effect of the precipitation or dissolution of all endmembers. For precipitation, mole fractions x_i are computed using Equation (I.5), which technically only applies at equilibrium. For dissolution, values of x_i are calculated from the actual abundances of each endmember present.

It should be noted that this method is currently valid only for rate expressions without exponents on the affinity term (i.e. with exponents m and n set to 1 in Equation B.5), and close to equilibrium for precipitation. This approach also implies that

$$k_{ss} = \sum_{i=1}^{n} (x_i k_i)$$

<div align="right">(I.12)</div>

and that

$$A_{ss} = \sum_{i=1}^{n} (A_i)$$

<div align="right">(I.13)</div>

where A_i is the surface area computed from the abundance of each endmember. Note that stoichiometric dissolution is obtained by using identical k_i values for all endmembers in a given solid solution.

Appendix J Implementation of the Hellmann and Tisserand (2006) Rate Law for Mineral Dissolution and Precipitation

J.1 Rate Expression

Hellmann and Tisserand (2006) published an improved rate equation for low albite dissolution in the aqueous phase;

$$r = kA\left(1 - e^{ng^m}\right)$$

(J.1)

where n and m are fitted parameters, and

$$g = \ln \frac{Q}{K}$$

(J.2)

They used an extensive and continuous set of experimental data relating the dissolution rate of low albite to the affinity of the reaction. The highly non-linear behavior of the rate equation precludes use of a classical TST rate law embodied in Eq. J.1, except when the affinity is less than ≈15 kJ/mol (Lasaga, 1998, p. 678 *ff*). Hellmann and Tisserand's equation better describes the dissolution rate of albite in the transition region between TST control and the generalized dissolution rate established far from equilibrium and independent of the affinity of reaction, a region characterized by most laboratory studies of aluminosilicate dissolution. Similar complex dissolution rate behavior has been observed for other minerals, e.g., gibbsite, labradorite and smectite (Lasaga and Luttge, 2001).

Although a theoretical basis exists for calculating the transition in dissolution rate between TST control, and control by etch pits for each mineral (Lasaga and Luttge, 2001), parameters are not available for many minerals. Hellmann and Tisserand (2006) reported the parameters n and m for albite, n = 9.75×10^{-5} and m = 3.74. We implemented this new rate law in TOUGHREACT, but it has not been well-tested. For some user's interest, we document the implementation below.

J.2 Implementation

Compared to TST rate law, only two records Miner-2 and Miner-2.1 in file chemical.inp needs to be modified as follows:

Miner-2

Variable: NAMIN, IKIN, IDISPRE, ISS, M1

Format: A, 4I (free format)

IKIN: =2 for this new rate law (=1 for TST rate law).

Other variables: are the same as the TST rate law

Miner-2.1

Variable: RKF, IDEP, CK1, CK2, EA, ACFDISS, BCFDISS, CCFDISS

Format: F, I, 6F (free format)

CK1 and CK2: the exponents n and m, respectively in Eq. (J.1) above.

Other variables: are the same as the TST rate law

An example for albite-low is given below:

```
'albite~low'         2     3     0     0
          2.7542e-13    2    9.75E-5  3.74 69.80  0.0  0.0  0.0
                  1
                  6.9183e-11   65.0    1   'h+'   0.457 ! acid mechnism
          1.0000e-12  0  9.75E-5  3.74  67.83  0.0  0.0  0.0   1.e-6   0
 0.0   0.   000.00
```

Appendix K Treatment of Cation Exchange under Water Unsaturated Conditions

Two models are used for cation exchange under water unsaturated conditions. The first model assumes cation exchange sites (CEC) remind constant as water saturation changes. In fact, the number of available exchange sites decreases as water saturation decreases. TOUGHREACT provides another option, the second model. The variation of exchange sites is addressed by simply scaling CEC by a factor, which is function of water saturation. TOUGHREACT can use a function $f(S_l)$ proposed by Liu et al. (1998) and is based on the change in reactive surface area with a change in saturation for fracture networks (see Appendix G):

$$f(S_l) = S_l^{(1+\gamma)}$$

(K.1)

where γ is an empirical coefficient. Both these functional forms are constrained in the range $0 \leq f(S_l) \leq 1$, and approach 0 as S_l approaches 0, and approach 1 as S_l approaches 1. Saturation values approaching 0 are usually not encountered, and are limited by the residual saturation in the capillary pressure curve. TOUGHREACT is, however, a nonisothermal code, and for boiling conditions, rocks can completely dry out. During complete dryout, Equations (K.1) become undefined at $S_l = 0$, and a lower limit must be placed on S_l to prevent this. For application under this condition, Sonnenthal et al. (2005) defined an effective residual saturation for reaction (S_{ar}), which is used in Equation (K.1) instead of S_l, and is expressed as

$$S_{ar} = \frac{S_l - S_m}{1 - S_m}$$

(K.2)

where S_m is the minimum liquid saturation for which reactions are considered and is generally set to a small saturation (such as 1×10^{-4}), to ensure that reactions take place until virtually no water is left (e.g., during dryout). Clearly, at a very low liquid saturation, the reactive exchange contacted by water is likely much smaller than the total sites. The dependence of reactive surface sites on water saturation is very complex in field-scale conditions. Additional investigations are needed to define the functional form of this relation.

Appendix L Heat Capacities and Thermal Conductivities of Rocks and Minerals

Rock Grain and Mineral Heat Capacities

In TOUGHREACT V3.0-OMP, temperature-dependent rock grain heat capacity coefficients (for use in the energy conservation equations) can be entered either directly into the ROCKS block of the flow input file, or calculated from individual mineral heat capacities. For the rock grain heat capacity ($C_{p,grain}$), two options are available. Option 1 (ihcplaw=1) uses the Holland and Powell (2011) polynomial, with units of J/kg/K instead of J/mol/K:

$$C_{p,grain} = a + bT + cT^{-2} + dT^{0.5}.$$
(L.1)

Option 2 (ihcplaw=2) uses a logarithmic expression for $C_{p,grain}$, as used in Hadgu et al. (2007), with T(°C) as follows:

$$C_{p,grain} = a\ln\left[T(C)\right] + b.$$
(L.2)

To calculate the rock grain heat capacity directly from the mineral abundances in each grid block, including changes as a result of mineral precipitation/dissolution, $C_{p,min}$ coefficients (a, b, c, d) for individual minerals are entered in an optional fourth line in the input thermodynamic data file (in J/mol/K). The format of this entry is given in the "Mineral" section of the thermodynamic data file input format description in the main section of this document. Mineral heat capacities ($C_{p,m}$ in J/mol/K) as a function of temperature (T in K) are calculated using the polynomial expression from Holland and Powell (2011):

$$C_{p,m} = a + bT + cT^{-2} + dT^{0.5}.$$
(L.3)

The energy conservation equation in TOUGHREACT is written in terms of rock grain heat capacities ($C_{p,grain}$) with units of J/kg/K, and therefore $C_{p,m}$ in J/mol/K must be converted to $C_{p,grain}$. First, the total moles of minerals (M_m) in each grid block (M_{tot}, moles/m³ medium) are calculated from the sum of the moles of individual minerals, as follows (*nm* is the total number of minerals present):

$$M_{tot} = \sum_{m=1}^{nm} M_m.$$
(L.4)

The mole fraction of each mineral (X_m) is then given by:

$$X_m = \frac{M_m}{M_{tot}}.$$ (L.5)

Prior to calculating the rock grain heat capacities, the rock grain heat capacity coefficients ($cf_{Cp,grain}$) are calculated from the mineral coefficients ($cf_{Cp,m}$), so they can be written to a file which can be later used in simulations without including reactive chemistry, as follows:

$$cf_{Cp,grain} = \sum_{m=1}^{nm} \left[cf_{Cp,m} \frac{X_m}{MW_m} \right],$$ (L.6)

where MW_m is the molecular weight of the mineral (kg/mol). Finally, the rock grain heat capacities are given by:

$$C_{p,grain} = \sum_{m=1}^{nm} \left[C_{p,m} \frac{X_m}{MW_m} \right].$$ (L.7)

Rock, Mineral, and Multiphase Thermal Conductivities

Temperature-dependent rock thermal conductivities can be calculated in TOUGHREACT V3.0-OMP using a choice of three formulations:

$$k_{T,rock} = \frac{a}{(350 + T(C))} + b \qquad \text{(Zoth and Hanel, 1988)}$$ (L.8)

$$k_{T,rock} = \frac{k_{Tref,rock}}{\left(a + bT(C) \right)\left(1 - \dfrac{c}{k_{Tref,rock}} \right)} \qquad \text{(Williams and Sass, 1996)}$$ (L.9)

$$k_{T,rock} = \frac{k_{Tref,rock}}{\left(a + T(C) \right)\left(b - \dfrac{c}{k_{Tref,rock}} \right)} \qquad \text{(Vosteen and Schellschmidt, 2003)}$$ (L.10)

where $k_{Tref,rock}$ is the saturated thermal conductivity at the reference temperature, entered in the usual location on line ROCKS.1.

Appendix M Heats of Reaction

Appendix N Single-Phase Wellbore Flow Model

Appendix O Utility Programs for the Thermodynamic Database

O.1 Converting from other databases

Description

Program DBCONV2 reads the thermodynamic database of either EQ3/6 v7.2b (data0.dat; Wolery, 1992), PHREEQC (phreeqc.dat; Parkhurst and Appelo, 1999), or SOLVEQ/CHILLER (soltherm.xxx; Reed, 1982 and 1998) formats the data for input into TOUGHREACT. The source code (dbconv2.f) is provided with the distribution files. For the most part, the conversion requires only reformatting of the same data values. However, the program also regresses input equilibrium constant values as a function of temperature in the form: $\log(K)_T = a * \ln(Tk) + b + c*Tk + d/Tk + e/Tk^2$ where Tk is temperature in degrees K. The program also assigns values of effective ionic radii to aqueous species by reading these values in a special input file (rej.dat). Currently, this file contains effective ionic radii from Helgeson et al. (1981; AJS, 1249-1516, Table 3). Radii of species for which data listed in rej.dat are computed as a function of ionic charge as shown in Table H.1-1 in Appendix H.

Input and output files:

The program needs to read in two input files and generates four output files. The names of input and output files are entered interactively when running the program. File contents and default names are as follows:

data0.dat	Main input file - original EQ3/6, PHREEQC or SOLVEQ/CHILLER thermodynamic database (the converter automatically detects the original file format).
rej.dat	Input data file containing effective ionic radii from Helgeson et al. (1981, AJS, 1249-1516, Table 3). The species listed in this file must have the same spelling as the species in the input thermodynamic database. If no match is found, rej values are computed based on ionic charge (See Table H.1-1 in Appendix H).
mvm0.dat	Mineral densities, used to compute molar volumes if these data are not available in the input database. References for these data are listed at the top of this file.
dbconv2.out	Main output file - converted database (for the file format, see Section 6.4 of this manual).
dump_aux.out	Separate subset of main output file containing converted data for auxiliary species only. To complete the conversion of the database, this file is to be manually inserted in dbconv2.out at the location indicated in that file.

checkfit.out   Print-plot file to visually check the quality of the log(K) regression. A user should always look at this file before using the output data.

checkdat.out   Printout of species for which one or more regressed log(K) value exceeds 0.1 log(K) units (generally, but not necessarily, indicating some problems with the regression).

For EQ3/6 conversions, the input file must have the format of EQ3/6 thermodynamic databases, with the following successive blocks of data. All these blocks are required in the input file and these data blocks must occur in the same order as shown below, otherwise input errors will occur:

```
+---------
basis species

+---------
auxiliary species

+---------
aqueous species

+---------
solid species

+---------
gases

+---------
solid solutions
```

To convert EQ3/6 files, the program will work only with input log(K) grids composed of eight values, at the following temperatures: 0, 25, 60, 100, 150, 200, 250, and 300°C. A log(K) value of 500 is interpreted as "no available data" and regression of log(K) values is not performed if at least one of log(K) value is set to 500. With PHREEQC databases, log(K) values are extrapolated only between 0 and 60°C using the van't Hoff equation and given enthalpy values, unless log(K) regression entries (-*analytic*) are present in the file. With SOLVEQ/CHILLER databases, log(K) values are regressed between 25 and 350°C, although log(K) values in the converted database are shown only up to 300°C.

O.2   Switching Basis (Primary) Species

Description

The program KSWITCH reads TOUGHREACT thermodynamic database entries and creates another identical set of entries with one of the component species "switched" with a derived species. For example, use KSWITCH to replace Al+++ (as a basis species) with new component species such as AlO_2^-.

Input data files and formats

One input file is needed (with default name thermok.dat, but any name can be chosen and input interactively). This file contains component species data, reaction stoichiometries and log(K) data entries that must have the same format as the entries for aqueous species, gases, and minerals in the TOUGHREACT thermodynamic database, including the same structure as the thermodynamic database (with a top record specifying temperature values for the log(K) data, then component (basis) species, derived species, minerals, and gases separated by records starting with 'null'). The entire thermodynamic database, or a subset of it, can be used as an input file. Also, any number of headers can appear at the top of the file before the temperature header. The remaining input is done interactively with self-explanatory prompts that ask for the names of input and output files, the species to switch (use the exact same spelling as in the input file), and the molecular weight of the switched species. The latter is used only for inclusion in the new component species entry and is not used in calculations. Note that the new component species must always be a derived species that is present in the input file. Also, only one switch is allowed for each run. For multiple switches, run the program more than once, reading the output of each run as input for the following run.

O.3 Regression of log(K) Data

Description

Program KREG is used to regress log(K) data in the thermodynamic database of TOUGHREACT as a function of temperature, and to generate records for aqueous species, minerals, and/or gases including the log(K) regression coefficients formatted for input into this thermodynamic database.

Input data files and formats

The names of input and output files are entered interactively when running the program. One input file (default name: kreg.dat) is required, containing: the first record identical to the first record of the thermodynamic database indicates the temperatures for which log(K) data are given, followed by records identical to those in the thermodynamic database for derived aqueous species, minerals, and/or gases. (3 records per entry: the first for stoichiometry, second for individual log(K) values, and the third for regression coefficients. The regression coefficients can be left blank, but the name of the species, mineral, or gas preceding the regression coefficients must be present). The entire thermodynamic database, with component (primary) species removed, can also be used as an input file.

O.4 Checking Mass and Charge Balances

Description

Program THERMOCHK reads the thermodynamic database of TOUGHREACT and checks the mass and charge balances of all reactions entered in that database. It does so by adding the molecular weights multiplied by stoichiometric coefficients (mass balance) and adding ionic charges multiplied by

stoichiometric coefficients (charge balance) of each specified reaction. The program then flags non-zero charge balances and mass balances greater than 5×10^{-5} times the molecular weight of the species/mineral/gas to which the reaction pertains.

Input data files and formats

The program needs to read in two input files and generates two output files. The names of input and output files are entered interactively when running the program. File contents and default names are as follows:

thermok.dat (default) Main input file (TOUGHREACT database to check)

molwt_aq.dat Input file with molecular weights of aqueous species, used only if this information is not already provided in the thermok.dat input file (i.e., as in earlier versions of the database).

thermochk.out Ouput file listing charge and mass balances for all reactions.

error.out Output file listing only those species, minerals, and gases for which reactions have non-zero charge balances and mass balances exceeding 5×10^{-5} times the molecular weight of the species, mineral, or gas in question.

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