

# **MIN3P User Guide**

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|          |   |               |
|----------|---|---------------|
| <b>1</b> | <b>INTRODUCTION .....</b>                               | <b>3.1-5</b>  |
| <b>2</b> | <b>INSTALLING AND RUNNING MIN3P .....</b>               | <b>3.1-6</b>  |
| <b>3</b> | <b>FILE STRUCTURE .....</b>                             | <b>3.1-8</b>  |
| 3.1      | INPUT FILES .....                                       | 3.1-8         |
| 3.2      | OUTPUT FILES .....                                      | 3.2-8         |
| <b>4</b> | <b>PROBLEM-SPECIFIC INPUT .....</b>                     | <b>3.2-13</b> |
| 4.1.1    | <i>prefix.dat file</i> .....                            | 3.2-13        |
| 4.1.2    | <i>Types of Simulations</i> .....                       | 3.2-13        |
| 4.1.3    | <i>Comment Lines and Notations</i> .....                | 3.2-14        |
| 4.1.4    | <i>Units</i> .....                                      | 3.2-14        |
| 4.2      | GLOBAL CONTROL PARAMETERS (DATA BLOCK 1) .....          | 4.2-15        |
| 4.2.1    | <i>Description of Data Block</i> .....                  | 4.2-15        |
| 4.2.2    | <i>Description of Input Parameters</i> .....            | 4.2-15        |
| 4.2.2.1  | 'global control parameters' .....                       | 4.2-15        |
| 4.2.2.2  | varsat_flow .....                                       | 4.2-15        |
| 4.2.2.3  | steady_flow .....                                       | 4.2-15        |
| 4.2.2.4  | fully_saturated .....                                   | 4.2-15        |
| 4.2.2.5  | reactive_transport .....                                | 4.2-15        |
| 4.2.3    | <i>Example Data File Input</i> .....                    | 4.2-16        |
| 4.2.4    | <i>Description of Example Input</i> .....               | 4.2-16        |
| 4.2.5    | <i>Additional Notes</i> .....                           | 4.2-16        |
| 4.3      | GEOCHEMICAL SYSTEM (DATA BLOCK 2) .....                 | 4.3-17        |
| 4.3.1    | <i>Description of Data Block</i> .....                  | 4.3-17        |
| 4.3.2    | <i>Description of Input Parameters</i> .....            | 4.3-17        |
| 4.3.2.1  | 'geochemical system' .....                              | 4.3-17        |
| 4.3.2.2  | 'components' .....                                      | 4.3-18        |
| 4.3.2.3  | 'database directory' .....                              | 4.3-18        |
| 4.3.2.4  | 'compute alkalinity' .....                              | 4.3-18        |
| 4.3.2.5  | 'define input units' .....                              | 4.3-18        |
| 4.3.2.6  | 'define temperature' .....                              | 4.3-19        |
| 4.3.2.7  | 'define temperature field' .....                        | 4.3-19        |
| 4.3.3    | <i>Example Data File Input</i> .....                    | 4.3-19        |
| 4.3.4    | <i>Description of Example Input</i> .....               | 4.3-21        |
| 4.3.4.1  | Additional Comments .....                               | 4.3-21        |
| 4.4      | SPATIAL DISCRETIZATION (DATA BLOCK 3) .....             | 4.4-21        |
| 4.4.1    | <i>Description of Data Block</i> .....                  | 4.4-21        |
| 4.4.2    | <i>Description of Input Parameters</i> .....            | 4.4-22        |
| 4.4.2.1  | 'spatial discretization' .....                          | 4.4-22        |
| 4.4.3    | <i>Example Data File Input</i> .....                    | 4.4-22        |
| 4.4.4    | <i>Description of Example Input</i> .....               | 4.4-23        |
| 4.4.5    | <i>Additional Notes</i> .....                           | 4.4-23        |
| 4.5      | TIME STEP CONTROL (DATA BLOCK 4) .....                  | 4.5-23        |
| 4.5.1    | <i>Description of Data Block</i> .....                  | 4.5-23        |
| 4.5.2    | <i>Description of Input Parameters</i> .....            | 4.5-24        |
| 4.5.2.1  | 'time step control - global system' .....               | 4.5-24        |
| 4.5.3    | <i>Example Data File Input</i> .....                    | 4.5-24        |
| 4.5.3.1  | Description of Example Input .....                      | 4.5-25        |
| 4.5.3.2  | Additional Comments .....                               | 4.5-25        |
| 4.6      | CONTROL PARAMETERS—LOCAL CHEMISTRY (DATA BLOCK 5) ..... | 4.6-25        |
| 4.6.1    | <i>Description of Section</i> .....                     | 4.6-25        |
| 4.6.2    | <i>Description of Input Parameters</i> .....            | 4.6-25        |
| 4.6.2.1  | 'control parameters - local geochemistry' .....         | 4.6-25        |

|          |   |         |
|----------|---|---------|
| 4.6.2.2  | 'newton iteration settings'                                 | 4.6-25  |
| 4.6.2.3  | 'output time unit'  | 4.6-26  |
| 4.6.2.4  | 'maximum ionic strength'                                    | 4.6-26  |
| 4.6.2.5  | 'minimum activity for h <sub>2</sub> o'                     | 4.6-26  |
| 4.6.3    | <i>Example Data File Input</i>                              | 4.6-27  |
| 4.6.3.1  | Additional Comments   | 4.6-27  |
| 4.7      | CONTROL PARAMETERS – VARIABLY SATURATED FLOW (DATA BLOCK 6) | 4.7-28  |
| 4.7.1    | <i>Description of Data Block</i>                            | 4.7-28  |
| 4.7.2    | <i>Description of Input Parameters</i>                      | 4.7-28  |
| 4.7.2.1  | 'control parameters - variably saturated flow'              | 4.7-28  |
| 4.7.2.2  | 'mass balance'  | 4.7-28  |
| 4.7.2.3  | 'input units for boundary and initial conditions'           | 4.7-28  |
| 4.7.2.4  | 'centered weighting'  | 4.7-28  |
| 4.7.2.5  | 'compute underrelaxation factor'                            | 4.7-29  |
| 4.7.2.6  | 'newton iteration settings'                                 | 4.7-29  |
| 4.7.2.7  | 'solver settings'   | 4.7-30  |
| 4.7.3    | <i>Example Data File Input</i>                              | 4.7-31  |
| 4.7.4    | <i>Description of Example Input</i>                         | 4.7-32  |
| 4.8      | CONTROL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 7)      | 4.8-32  |
| 4.8.1    | <i>Description of Section</i>                               | 4.8-32  |
| 4.8.2    | <i>Description of Input Parameters</i>                      | 4.8-32  |
| 4.8.2.1  | 'mass balance'  | 4.8-33  |
| 4.8.2.2  | 'spatial weighting'   | 4.8-33  |
| 4.8.2.3  | 'activity update settings'                                  | 4.8-34  |
| 4.8.2.4  | 'tortuosity correction'                                     | 4.8-34  |
| 4.8.2.5  | 'degassing'   | 4.8-34  |
| 4.8.2.6  | 'update porosity'   | 4.8-34  |
| 4.8.2.7  | update permeability'  | 4.8-35  |
| 4.8.2.8  | 'newton iteration settings'                                 | 4.8-35  |
| 4.8.2.9  | 'solver settings'   | 4.8-36  |
| 4.8.3    | <i>Data File Input</i>                                      | 4.8-36  |
| 4.8.4    | <i>Description of Example Input</i>                         | 4.8-37  |
| 4.9      | OUTPUT CONTROL (DATA BLOCK 8)                               | 4.9-39  |
| 4.9.1    | <i>Description of Data Block</i>                            | 4.9-39  |
| 4.9.2    | <i>Description of Input Parameters</i>                      | 4.9-39  |
| 4.9.2.1  | 'output control'  | 4.9-39  |
| 4.9.2.2  | 'output of spatial data'                                    | 4.9-39  |
| 4.9.2.3  | 'output of transient data'                                  | 4.9-39  |
| 4.9.2.4  | 'output in terms of depth'                                  | 4.9-40  |
| 4.9.3    | <i>Example Data File Input</i>                              | 4.9-40  |
| 4.9.4    | <i>Description of Example Input</i>                         | 4.9-41  |
| 4.10     | PHYSICAL PARAMETERS: POROUS MEDIUM (DATA BLOCK 9)           | 4.10-41 |
| 4.10.1   | <i>Description of Data Block</i>                            | 4.10-41 |
| 4.10.2   | <i>Description of Input Parameters</i>                      | 4.10-41 |
| 4.10.2.1 | 'physical parameters - porous medium'                       | 4.10-41 |
| 4.10.2.2 | 'number and name of zone'                                   | 4.10-41 |
| 4.10.3   | <i>Example Data File Input</i>                              | 4.10-42 |
| 4.10.4   | <i>Description of Example Input</i>                         | 4.10-43 |
| 4.11     | PHYSICAL PARAMETERS-VARIABLY SATURATED FLOW (DATA BLOCK 10) | 4.11-43 |
| 4.11.1   | <i>Description of Data Block</i>                            | 4.11-43 |
| 4.11.2   | <i>Description of Input Parameters</i>                      | 4.11-44 |
| 4.11.2.1 | 'physical parameters - porous medium'                       | 4.11-44 |
| 4.11.2.2 | 'hydraulic conductivity in ?-direction'                     | 4.11-44 |
| 4.11.2.3 | 'specific storage coefficient'                              | 4.11-44 |
| 4.11.2.4 | 'soil hydraulic function parameters'                        | 4.11-44 |
| 4.11.3   | <i>Example Data File Input</i>                              | 4.11-45 |
| 4.11.4   | <i>Description of Example Input</i>                         | 4.11-46 |

|          |   |                |
|----------|---|----------------|
| 4.11.5   | Additional Comments.....  | 4.11-47        |
| 4.12     | PHYSICAL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 11).....       | 4.12-47        |
| 4.12.1   | Description of Data Block .....                                     | 4.12-47        |
| 4.12.2   | Description of Input Parameters .....                               | 4.12-47        |
| 4.12.2.1 | 'physical parameters – porous medium'.....                          | 4.12-47        |
| 4.12.2.2 | 'diffusion coefficients' .....                                      | 4.12-47        |
| 4.12.2.3 | 'dispersivity' .....  | 4.12-48        |
| 4.12.3   | Example Data File Input.....  | 4.12-48        |
| 4.12.4   | Description of Example Input.....                                   | 4.12-49        |
| 4.12.5   | Additional Comments.....  | 4.12-49        |
| 4.13     | INITIAL CONDITION - VARIABLY SATURATED FLOW (DATA BLOCK 12).....    | 4.13-49        |
| 4.13.1   | Description of Data block.....                                      | 4.13-49        |
| 4.13.2   | Description of Input Parameters .....                               | 4.13-50        |
| 4.13.2.1 | 'initial condition – variably saturated flow' .....                 | 4.13-50        |
| 4.13.2.2 | 'initial condition' .....   | 4.13-50        |
| 4.13.2.3 | extent of zone' .....   | 4.13-50        |
| 4.13.3   | Example Data File Input.....  | 4.13-52        |
| 4.13.4   | Description of Example Input.....                                   | 4.13-53        |
| 4.13.5   | Additional Comments.....  | 4.13-53        |
| 4.14     | BOUNDARY CONDITIONS - VARIABLY SATURATED FLOW (DATA BLOCK 13) ..... | 4.14-53        |
| 4.14.1   | Description of Data Block .....                                     | 4.14-53        |
| 4.14.2   | Description of Input Parameters .....                               | 4.14-54        |
| 4.14.2.1 | 'boundary conditions – variably saturated flow' .....               | 4.14-54        |
| 4.14.2.2 | 'boundary type'.....  | 4.14-54        |
| 4.14.2.3 | 'extent of zone' .....  | 4.14-54        |
| 4.14.3   | Example Data File Input.....  | 4.14-56        |
| 4.14.4   | Description of Example Input.....                                   | 4.14-57        |
| 4.14.5   | Additional Comments.....  | 4.14-57        |
| 4.15     | INITIAL CONDITION – BATCH REACTIONS (DATA BLOCK 14).....            | 4.15-57        |
| 4.15.1   | Description of Data Block .....                                     | 4.15-57        |
| 4.15.2   | Description of Input Parameters .....                               | 4.15-59        |
| 4.15.2.1 | 'initial condition – local geochemistry' .....                      | 4.15-59        |
| 4.15.2.2 | 'kinetic batch simulation' .....                                    | 4.15-59        |
| 4.15.2.3 | Concentration Input .....   | 4.15-59        |
| 4.15.2.4 | 'sorption parameter input' .....                                    | 4.15-60        |
| 4.15.2.5 | 'mineral input'.....  | 4.15-61        |
| 4.15.3   | Example Data File Input.....  | 4.15-67        |
| 4.15.4   | Description of Example Input.....                                   | 4.15-70        |
| 4.15.5   | Additional Comments.....  | 4.15-70        |
| 4.16     | INITIAL CONDITION – REACTIVE TRANSPORT (DATA BLOCK 15).....         | 4.16-70        |
| 4.16.1   | Description of Section.....   | 4.16-70        |
| 4.16.2   | Description of Input Parameters .....                               | 4.16-71        |
| 4.16.2.1 | 'initial condition – reactive transport' .....                      | 4.16-71        |
| 4.16.2.2 | 'extent of zone' .....  | 4.16-71        |
| 4.16.3   | Example Data File Input.....  | 4.16-71        |
| 4.16.4   | Description of Example Input.....                                   | 4.16-72        |
| 4.16.5   | Additional Comments.....  | 4.16-72        |
| 4.17     | BOUNDARY CONDITIONS - REACTIVE TRANSPORT (DATA BLOCK 16).....       | 4.17-72        |
| 4.17.1   | Description of Section.....   | 4.17-72        |
| 4.17.2   | Description of Input Parameters .....                               | 4.17-72        |
| 4.17.3   | Example Data File Input.....  | 4.17-73        |
| 4.17.4   | Description of Example Input.....                                   | 4.17-74        |
| 4.17.5   | Additional Comments.....  | 4.17-74        |
| <b>5</b> | <b>DATABASE.....</b>  | <b>4.17-75</b> |
| 5.1      | COMPONENTS.....   | 5.1-75         |

|         |  |        |
|---------|--|--------|
| 5.1.1   | <i>comp.db</i> s .....   | 5.1-75 |
| 5.1.1.1 | aqueous components .....   | 5.1-75 |
| 5.1.1.2 | non-aqueous components .....   | 5.1-75 |
| 5.1.2   | <i>Adding new components</i> .....   | 5.1-76 |
| 5.2     | COMPLEXATION REACTIONS .....   | 5.2-76 |
| 5.2.1.1 | Line 1. ....   | 5.2-76 |
| 5.2.1.2 | Line 2. ....   | 5.2-76 |
| 5.2.2   | <i>Adding Complexes</i> .....  | 5.2-77 |
| 5.3     | GAS EXCHANGE REACTIONS .....   | 5.3-77 |
| 5.4     | ION EXCHANGE AND SORPTION REACTIONS .....  | 5.4-77 |
| 5.5     | EQUILIBRIUM REDOX REACTIONS AND KINETICALLY-CONTROLLED INTRA-AQUEOUS REACTIONS<br>5.5-78 |        |
| 5.6     | MINERAL DISSOLUTION-PRECIPITATION REACTIONS.....   | 5.6-80 |
| 5.6.1   | <i>Surface-controlled rate expressions</i> .....   | 5.6-80 |
| 5.6.2   | <i>Diffusion-controlled rate expression</i> .....  | 5.6-83 |

## 1 INTRODUCTION

The MIN3P code is a multicomponent reactive transport model for variably saturated porous media in one, two or three spatial dimensions. Advective-dispersive transport in the aqueous phase, as well as diffusive gas transport can be considered. Darcy velocities are calculated internally using a variably-saturated flow module. The model formulation is based on the global implicit solution approach [Steefel and Lasaga,1994], which considers reaction and transport processes simultaneously. This formulation enforces a global mass balance between solid, surface, dissolved and gaseous species and thus facilitates the investigation of the interactions of reaction and transport processes. The model can also be used as a batch model for equilibrium speciation problems, kinetic batch problems or for the generation of pC-pH-diagrams.

MIN3P is characterized by a high degree of flexibility with respect to the definition of the geochemical reaction network to facilitate the application of the model to a wide range of hydrogeological and geochemical problems. Chemical processes included are homogeneous reactions in the aqueous phase, such as complexation and oxidation-reduction reactions, as well as heterogeneous reactions, such as ion exchange, surface complexation, mineral dissolution-precipitation and gas exchange reactions. Reactions within the aqueous phase and dissolution-precipitation reactions can be considered as equilibrium or kinetically-controlled processes. The model formulation is conceptually similar to the reactive transport models developed by Steefel and Lasaga [1994] and Lichtner [1996].

A new, general framework for kinetically-controlled intra-aqueous and mineral dissolution-precipitation reactions was developed. All kinetically-controlled reactions can be described as reversible or irreversible reaction processes. Different reaction mechanisms for dissolution-precipitation reactions are considered, which can be subdivided into surface- and transport-controlled reactions [Berner, 1978, Steefel and Lasaga, 1994]. This approach allows the consideration of a large number of rate expressions reported in the literature. Related reaction and rate parameters can be incorporated into the model through an accompanying database. The model is primarily designed for problems involving inorganic chemistry, but reactions involving organic chemicals can also be accommodated. Microbially-mediated reactions can be described using a multiplicative Monod approach.

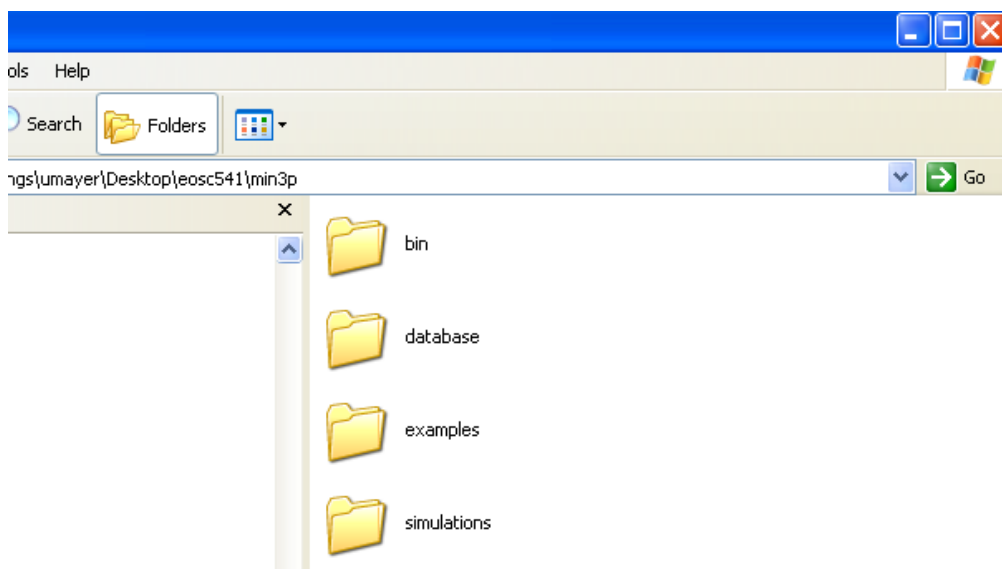
This user guide describes the program installation followed by a brief description of the database and the input file structure, as well as the content of the output files. In the next section a description of the problem-specific model input is provided. The content of the database is described and the addition of reactions to the database is outlined. (Several example applications will be provided in the complete version of the user guide.)



## 2 INSTALLING AND RUNNING MIN3P

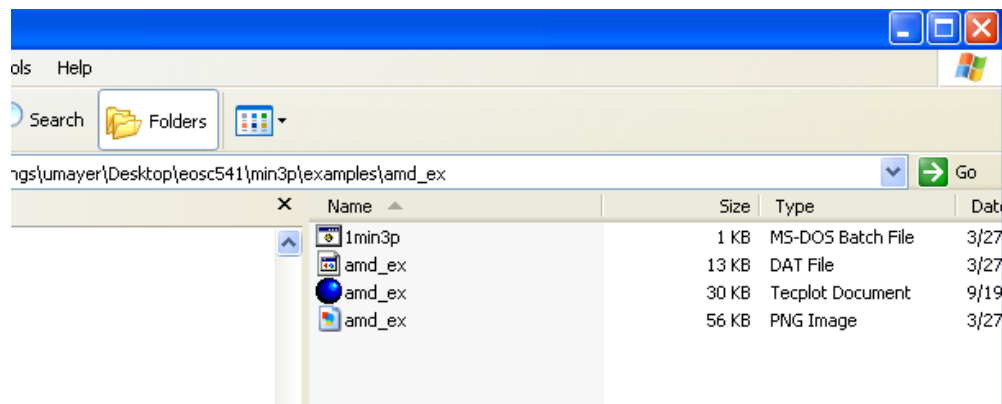
The following description is based on the assumption that the program will be installed on a PC. The package can be installed on any drive. This guide assumes that the program will be installed on the d-drive, if this is not the case the drive letter d must be replaced by the actual drive letter:

Extract the program and example files at any location on your computer. The program will extract into a main directory “min3p” that contains a number of subdirectories.



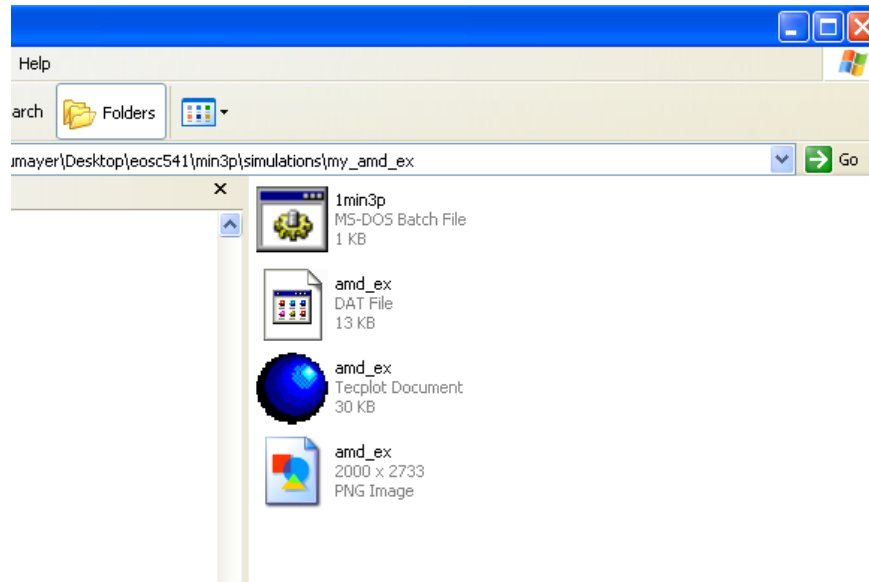
The “bin” directory includes the min3p executable. The “database” directory includes the database files, the “examples” directory includes a set of worked examples, the simulations directory is empty and is dedicated for new min3p simulations.

The program can be started using a batch file (1min3p.bat) that is included in each example directory.



To execute the program, double click on “1min3p”. A Dos window with a welcome screen will appear. When prompted, enter the problem specific file name, in the example above: amd\_ex, then press enter and the simulation will start.

Due to the potential large number of output files generated by the program, it is highly recommended to create a directory for each new simulation. You can simply copy an existing example to a new location in the “simulations” directory, and modify the input file using notepad, wordpad or a similar ascii text editor (in this case the amd\_ex.dat file). Start the simulation as described above:



**IMPORTANT:** If you want to run the simulations elsewhere than in the “simulations” directory, you will have to update the path to the database files in the input file (\*.dat file) and the path to the executable in the 1min3p.bat file. This can be avoided by sticking to the simulations directory.

### 3 FILE STRUCTURE

Required input files can be subdivided into problem specific input files and database files. Additional species or reactions may be specified in the database files. When changing the database files for a specific problem, an original copy of the database should always be maintained (see Section 5 on how to maintain the database and on how to add additional components, species, or reactions to the database).

#### 3.1 INPUT FILES

The input `prefix.dat`, where `prefix` is a problem name with up to 72 characters contains the problem-dependent input. This file together with all database files is required to operate the model. It is optional to specify a depth-dependent temperature field or an initial condition for transient groundwater flow problems. These data may be provided in the files `prefix.tem` (temperature) and `prefix.ivs` (initial condition variably-saturated flow).

| Type                         | File name                 | Description                           | Requirement |
|------------------------------|---------------------------|---------------------------------------|-------------|
| problem specific input files | <code>prefix.dat</code>   | General problem specific input        | Required    |
|                              | <code>prefix.tem</code>   | Depth dependent temperature field     | Optional    |
|                              | <code>prefix.ivs</code>   | Initial condition for flow simulation | Optional    |
| database files               | <code>comp.dbs</code>     | Components                            | Required    |
|                              | <code>complex.dbs</code>  | Aqueous complexation                  | Required    |
|                              | <code>redox.dbs</code>    | Oxidation-reduction                   | Required    |
|                              | <code>gases.dbs</code>    | Gas dissolution-exsolution            | Required    |
|                              | <code>sorption.dbs</code> | Ion exchange                          | Required    |
|                              | <code>mineral.dbs</code>  | Mineral dissolution-precipitation     | Required    |

Table 1: Input file and database files

#### 3.2 OUTPUT FILES

All output files are described in the file `prefix_o.fls`. This file contains the file names, provides a brief description of the content of the files and lists the parameters contained in the files. It is generated on program-execution. The most important output files are summarized in the following tables. For the remaining output files it is referred to the file `prefix_o.fls`.

| File name    | Description  | TECPLOT Header |
|--------------|--|----------------|
| prefix_o.gen | General problem specific output, contains feed-back from input file and results of batch simulations including the equilibration of background and source water chemistry<br>Output format: assorted<br>Suffix meaning: <b>gen</b> = <b>general</b>      | N              |
| prefix.log   | run-specific information on convergence and trouble shooting<br>Output format: assorted<br>Suffix meaning: <b>log</b> = <b>logbook</b>   | N              |
| prefix_x.gsp | hydraulic head, pressure head, water and gas saturations, moisture and gas contents at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsp</b> = <b>global/spatial/pressure</b> | Y              |
| prefix_x.vel | interfacial velocities at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), $v_x$ , $(v_y)$ , $(v_z)$<br>Suffix meaning: <b>vel</b> = <b>velocities</b>  | Y              |

Table 2: Output files – general model output and flow solution

| File name    | Description   | TECPLOT Header |
|--------------|---|----------------|
| prefix_x.gst | total aqueous component concentrations at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gst</b> = <b>global/spatial/total aqueous component concentrations</b>           | Y              |
| prefix_x.gsc | aqueous species concentrations at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsc</b> = <b>global/spatial/species concentrations</b>                                   | Y              |
| prefix_x.gsi | reaction rates of intra-aqueous kinetic reactions at output time x – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsi</b> = <b>global/spatial/intra-aqueous kinetic reactions</b>                               | Y              |
| prefix_x.gsm | master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsm</b> = <b>global/spatial/master variables</b> | Y              |

|               |  |   |
|---------------|--|---|
| prefix_x.gsg  | partial gas pressures at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsg</b> = global/spatial/partial <b>g</b> as pressures | Y |
| prefix_x.gsgr | degassing rates at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsgr</b> – global/spatial/degassing/rates                    | Y |
| prefix_x.gsv  | mineral volume fractions at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsv</b> – global/spatial/volume fractions           | Y |
| prefix_x.gsb  | surface species at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsb</b> – global/spatial/sorbed species                      | Y |
| prefix_x.gss  | mineral saturation indices at output time x (0 = initial condition) – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gss</b> – global/spatial/saturation indices       | Y |

Table 3: Output files – reactive transport – contour data.

| File name    | Description  | TECPLOT Header |
|--------------|--|----------------|
| prefix_x.gsd | mineral dissolution-precipitation rates at output time x – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsd</b> = global/spatial/dissolution-precipitation rates             | Y              |
| prefix_x.gsx | saturation indices of excluded minerals at output time x – contour data<br>Output format: x,(y),(z), parameter values<br>Suffix meaning: <b>gsd</b> = global/spatial/excluded minerals                           | Y              |
| prefix_x.gbt | total aqueous component concentrations at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbt</b> = global/breakthrough/total aqueous component concentrations | Y              |
| prefix_x.gbc | aqueous species concentrations at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbc</b> = global/breakthrough/species concentrations                         | Y              |

|               |  |   |
|---------------|--|---|
| prefix_x.gbi  | reaction rates of intra-aqueous kinetic reactions at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbi</b> = global/breakthrough/intra-aqueous kinetic reactions       | Y |
| prefix_x.gbm  | master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbm</b> = global/breakthrough/master variables | Y |
| prefix_x.gbg  | partial gas pressures at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbg</b> = global/breakthrough/partial gas pressures   | Y |
| prefix_x.gbgr | degassing rates at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbgr</b> – global/breakthrough/degassing/rates  | Y |
| prefix_x.gbv  | mineral volume fractions at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbv</b> – global/breakthrough/volume fractions   | Y |
| prefix_x.gbb  | surface species at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbb</b> – global/breakthrough/sorbed species  | Y |
| prefix_x.gbs  | mineral saturation indices at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbs</b> – global/breakthrough/saturation indices   | Y |
| prefix_x.gbd  | mineral dissolution-precipitation rates at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbd</b> = global/breakthrough/dissolution-precipitation rates                 | Y |
| prefix_x.gbx  | saturation indices of excluded minerals at output location x – transient data<br>Output format: time, parameter values<br>Suffix meaning: <b>gbx</b> = global/breakthrough/excluded minerals                               | Y |

Table 4: Output files – reactive transport – transient data

| File name | Description | TECPLOT Header |
|-----------|-------------|----------------|
|-----------|-------------|----------------|

|               |  |   |
|---------------|--|---|
| prefix_x.lbt  | total aqueous component, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbt</b> = local/breakthrough/total aqueous component concentrations                           | Y |
| prefix_x.lbc  | aqueous species concentrations, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbc</b> = local/breakthrough/species concentrations                                    | Y |
| prefix_x.lbi  | reaction rates of intra-aqueous kinetic reactions, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbi</b> = local/breakthrough/intra-aqueous kinetic reactions        | Y |
| prefix_x.lbm  | master variables (pH, pe, Eh, ionic strength, alkalinity, temperature) , local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbm</b> = local/breakthrough/master variables | Y |
| prefix_x.lbg  | partial gas pressures, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lb g</b> = local/breakthrough/partial gas pressures   | Y |
| prefix_x.lbgr | degassing rates, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbgr</b> – local/breakthrough/degassing/rates   | Y |
| prefix_x.lbv  | mineral volume fractions, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbv</b> – local/breakthrough/volume fractions  | Y |
| prefix_x.lbb  | surface species, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbb</b> – local/breakthrough/sorbed species   | Y |
| prefix_x.lbs  | mineral saturation indices, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbs</b> – local/breakthrough/saturation indices  | Y |
| prefix_x.lbd  | mineral dissolution-precipitation rates, local geochemistry – transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbd</b> = local/breakthrough/dissolution-precipitation rates                  | Y |

|              |  |   |
|--------------|--|---|
| prefix_x.lbx | saturation indices of excluded minerals, local geochemistry<br>– transient data, or pC-pH-data<br>Output format: time or pH, parameter values<br>Suffix meaning: <b>lbx</b> = local/breakthrough/excluded minerals | Y |
|--------------|--|---|

Table 5: Output files – local geochemistry

## 4 PROBLEM-SPECIFIC INPUT

### 4.1.1 prefix.dat file

The problem-specific input file (`prefix.dat`) is composed of a series of sections or data blocks. Each data block contains specific input information and may contain a series of sub-sections or sub-blocks. Each data block is bounded by a keyword at the top and a 'done' statement at the bottom. There are a total of 16 data blocks:

| Data Block | Keyword   |
|------------|---|
| 1          | 'global control parameters'                     |
| 2          | 'geochemical system'                            |
| 3          | 'spatial discretization'                        |
| 4          | 'time step control'                             |
| 5          | 'control parameters - local chemistry'          |
| 6          | 'control parameters - variably saturated flow'  |
| 7          | 'control parameters - reactive transport'       |
| 8          | 'output control'                                |
| 9          | 'physical parameters - porous medium'           |
| 10         | 'physical parameters - variably saturated flow' |
| 11         | 'physical parameters - reactive transport'      |
| 12         | 'initial condition - variably saturated flow'   |
| 13         | 'boundary condition - variably saturated flow'  |
| 14         | 'initial condition - local chemistry'           |
| 15         | 'boundary conditions - reactive transport'      |
| 16         | 'initial condition - reactive transport'        |

Table 6: Data blocks for problem specific input file

The sections can appear in any order in the input file, and the order of the subsections within each section can also vary.

### 4.1.2 Types of Simulations

MIN3P can perform four general types of simulations. They are: batch, steady-state flow, transient flow, and flow and reactive transport simulations.



| Simulation Type             | Description  | Examples   |
|-----------------------------|--|--|
| Batch                       | No-flow modeling of geochemical processes            | Speciation calculations, and Kinetic batch experiments |
| Steady-State Flow           | 1,2, or 3-Dimensional flow modelling at steady-state | Flow in column, x-section, or 3-D domain               |
| Transient Flow              | As above but with conditions changing with time      | As above but with conditions changing with time        |
| Flow and Reactive Transport | As above but with geochemical reactions              | Columns tests and Groundwater plume evolution          |

Table 7: Types of simulations

Depending on the type of simulation to be conducted, certain subsections and even entire sections are optional, while others, defining the essential problem-specific parameters, are Required. Table 8 summarizes the input section requirements for each simulation type (R = Required, O = optional, N = not used):

| Simulation type             | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|-----------------------------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|
| batch                       | R | R | N | N | O | N | N | N | N | N  | N  | N  | N  | R  | N  | N  |
| steady flow                 | R | N | R | N | N | O | N | O | R | R  | N  | R  | R  | N  | N  | N  |
| transient flow              | R | N | R | R | N | O | N | O | R | R  | N  | R  | R  | N  | N  | N  |
| flow and reactive transport | R | R | R | R | O | O | O | O | R | R  | R  | R  | R  | N  | R  | R  |

Table 8: Input requirements for simulation types

#### 4.1.3 Comment Lines and Notations

Each line starting with an exclamation mark (!) is a comment line and will not be read by the program. The user is encouraged to add comments to the input file whenever deemed necessary. When the program reads the input file, it searches for the required parameter and then moves to the next line. Therefore, any text found to the right of the required parameter will be ignored and notes can be added without effecting the input file.

#### 4.1.4 Units

All input is in SI-units, unless otherwise noted.

## 4.2 GLOBAL CONTROL PARAMETERS (DATA BLOCK 1)

### 4.2.1 Description of Data Block

In this data block the problem title is read and the type of simulation to be conducted is specified. The options are:

- Geochemical batch simulation
- Flow simulation (transient or steady-state and fully- or variably-saturated)
- Flow and reactive transport simulation (transient or steady-state and fully or variably saturated)

### 4.2.2 Description of Input Parameters

#### 4.2.2.1 'global control parameters'

The input is initiated with the header defining the section name ('global control parameters'). In the next line the problem title must be specified (up to 72 characters in quotes). To specify what type of simulation is to be performed, four true/false statements must be specified in the following four input lines:

#### 4.2.2.2 varsat\_flow

This statement determines if a flow simulation is to be performed.

#### 4.2.2.3 steady\_flow

This statement determines if the flow simulation is to be steady-state or transient.

#### 4.2.2.4 fully\_saturated

This statement specifies if the simulation is to be variably saturated or fully saturated.

#### 4.2.2.5 reactive\_transport

This statement specifies if the simulation is to involve reactive transport. The model can also be used to perform geochemical batch simulations, this requires that all true/false statements are set to false.

The table below shows the nine types of simulations possible and indicates the required true/false statements for each scenario.

| Scenarios   | True/False Parameters |             |                 |                    |
|---|-----------------------|-------------|-----------------|--------------------|
|   | varsat_flow           | steady_flow | fully_saturated | reactive_transport |
| Batch   | .false.               | .false.     | .false.         | .false.            |
| Steady-state, Fully-saturated Flow                          | .true.                | .true.      | .true.          | .false.            |
| Transient, Fully-saturated Flow                             | .true.                | .false.     | .true.          | .false.            |
| Steady-state, Variably-saturated Flow                       | .true.                | .true.      | .false.         | .false.            |
| Transient, Variably-saturated Flow                          | .true.                | .false.     | .false.         | .false.            |
| Steady-state, Fully-saturated Flow, Reactive Transport      | .true.                | .true.      | .true.          | .true.             |
| Transient, Fully-saturated Flow, w/ Reactive Transport      | .true.                | .false.     | .true.          | .true.             |
| Steady-state, Variably-saturated Flow w/ Reactive Transport | .true.                | .true.      | .false.         | .true.             |
| Transient, Variably-saturated Flow w/ Reactive Transport    | .true.                | .false.     | .false.         | .true.             |

Table 9: Parameter settings for simulation types

### 4.2.3 Example Data File Input

```

! -----
'global control parameters'
'Flow Simulation - Nickel Rim - Reactive Wall - Base Case'
.true.                ;varsat_flow
.true.                ;steady_flow
.true.                ;fully_saturated
.false.               ;reactive_transport
'done'

```

### 4.2.4 Description of Example Input

The example input defines a steady state flow simulation under fully-saturated conditions; reactive transport is excluded. The title is used to identify run-specific information.

### 4.2.5 Additional Notes

It is recommended that a modeling problem be approached in a step by step manner. For

example, the user can start by simulate flow until satisfied with the results, then perform initial geochemical simulations using the batch module. In a final step the reactive transport simulation can be conducted. This stepwise approach limits the number of new parameters for each simulation and will make troubleshooting much easier.

## 4.3 GEOCHEMICAL SYSTEM (DATA BLOCK 2)

### 4.3.1 Description of Data Block

All problem-specific geochemical species and reactions are defined in this data block. In addition, the input units the temperature, the redox master variable, and the database to be used for the simulation, can also be specified.

### 4.3.2 Description of Input Parameters

#### 4.3.2.1 'geochemical system'

The data block 'geochemical system' is composed of a series of sub-blocks. The sub-block 'components' is required for all simulations. The all possible sub-blocks are tabulated below.

| Name*                             | Description  | Database File  | Required? |
|-----------------------------------|--|----------------|-----------|
| 'components'                      | Basic species to be considered   | 'comp.dbs'     | Y         |
| 'secondary aqueous species'       | Equilibrium complexation reactions   | 'complex.dbs'  | N         |
| 'redox couples'                   | Equilibrium oxidation-reduction reactions  | 'redox.dbs'    | N         |
| 'gases'                           | Gas dissolution- exsolution reactions  | 'gases.dbs'    | N         |
| 'sorbed species'                  | Ion exchange reactions   | 'sorption.dbs' | N         |
| 'minerals'                        | Kinetically-controlled mineral dissolution precipitation reactions                           | 'mineral.dbs'  | N         |
| 'excluded minerals'               | Excluded mineral phases, do not participate in reactions, but saturation index is calculated | 'mineral.dbs'  | N         |
| 'intra-aqueous kinetic reactions' | Kinetically-controlled complexation and oxidation reduction reactions                        | 'redox.dbs'    | N         |
| 'compute alkalinity'              | Used to calculate and output alkalinity  | none           | N         |

|   |                          |            |   |
|---|--------------------------|------------|---|
| 'define input units'  | Define input units       | none       | N |
| 'define temperature'  | Define temperature       | none       | N |
| 'define temperature field'  | Define temperature field | prefix.tem | N |
| *All keyword headings must appear on a single line in the input file. Separation by a <Return> will result in destruction of the world as we know it. |                          |            |   |

Table 10: Summary of input parameters for data block 'geochemical system'

Each of these entries is considered a sub-block and is followed by the number of the species/reactions and by the names of these species (see example input). The names of the reactions or species can be found in the database files listed above. All specified reactions and species must be composed of components specified for that simulation.

#### 4.3.2.2 'components'

This sub-block requires the specification of the number and names of components. Possible choices for components are defined in the database `comp.dbs`. The components are the basis species for the geochemical system considered. All other species or reactions consist of or involve one or more components.

#### 4.3.2.3 'database directory'

The geochemical database to be used for the simulation must be specified following the text string 'database directory'. The full path of the database must be entered, e.g.:

```
'database directory'
'd:\min3p\database\default'
```

The 'default' database is based on the databases from MINTEQA2 (Allison et al., 1991) and WATEQ4F (Ball and Nordstrom, 1991).

#### 4.3.2.4 'compute alkalinity'

If desired, the program calculates alkalinity, carbonate and non-carbonate alkalinity and writes the results to the files `prefix_x.gsm` and `prefix_x.gbm`. Alkalinity calculations are activated with the command:

```
'compute alkalinity'
```

#### 4.3.2.5 'define input units'

By default, the program assumes that all chemical data will be provided in units  $\text{mol L}^{-1}$   $\text{H}_2\text{O}$ . Other possible input units are  $\text{mg L}^{-1}$ ,  $\text{mmol L}^{-1}$  and  $\text{g L}^{-1}$ . For example:

```
'define input units'
'mg/l'
```

will specify input of aqueous concentrations in units  $\text{mg L}^{-1}$ .

#### 4.3.2.6 'define temperature'

By default, all geochemical calculations are conducted at standard temperature ( $25^{\circ}\text{C}$ ). Other temperatures can be specified using, for example:

```
'define temperature'
10.0
```

#### 4.3.2.7 'define temperature field'

It is also possible to define a depth and time dependent temperature field. This option is activated using the command:

```
'define temperature field'
```

If activated, the program expects that a file with the name `prefix.tem` exists. This file must follow the format:

|       |           |           |     |           |
|-------|-----------|-----------|-----|-----------|
| N     | $z_1$     | $z_2$     | ... | $z_N$     |
| $t_1$ | $T_{1,1}$ | $T_{1,2}$ | ... | $T_{1,N}$ |
| $t_2$ | $T_{2,1}$ | $T_{2,2}$ | ... | $T_{2,N}$ |
| ...   | ...       | ...       | ... | ...       |
| $t_M$ | $T_{M,1}$ | $T_{M,2}$ | ... | $T_{M,N}$ |

where  $N$  is the number of temperature points,  $z_1$  to  $z_N$ , are the depth coordinates of the temperature points,  $t_1$ – $t_M$ , are the times of observation and  $T_{1,1}$  to  $T_{M,N}$  are the observed temperatures. The program interpolates these temperature values over the spatial solution domain and updates the temperature while advancing in time. Once the last specified input time is reached, the program reverts to the first input time. This allows the simulation of temperature effects on geochemical reactions due to seasonal changes by specifying only one yearly temperature cycle. An example temperature file can be found in the Appendix

#### 4.3.3 Example Data File Input

```
! -----
'geochemical system'

'components'
9                                ;number of components (nc-1)
    'ca+2'                      ;component names
    'co3-2'
    'h+1'
```

```

    'fe+2'
    'fe+3'
    'so4-2'
    'hs-1'
    'o2(aq)'
    'ch2o'

'redox couples'
1                                     ;number of redox couples
    'fe+2' 'fe+3'                   ;names of redox couples

'secondary aqueous species'
26                                  ;number of secondary aqueous species
    'oh-'                           ;names of secondary aqueous species
    'caoh+'
    'cahco3+'
    'caco3aq'
    'caso4aq'
    'cahso4+'
    'feoh+'
    'feoh3-1'
    'feso4aq'
    'fehso4+'
    'fehco3+'
    'feco3aq'
    'feoh2aq'
    'fe(hs)2aq'
    'fe(hs)3-'
    'feoh+2'
    'feso4+'
    'fehso42+'
    'feoh2+'
    'feoh3aq'
    'feoh4-'
    'fe(so4)2-'
    'hco3-'
    'h2co3aq'
    'hso4-'
    'h2saq'

'gases'
2                                     ;number of gases
    'o2(g)'                         ;names of gases
    'co2(g)'

'minerals'
5                                     ;number of minerals
    'pyrite'                        ;mineral names
    'calcite'
    'ferrihydrite'
    'siderite'
    'gypsum'

'excluded minerals'
2
    'goethite'
    'aragonite'

'intra-aqueous kinetic reactions'
1                                     ;number of intra-aqueous reactions
    'so4-reduction'                 ;names of intra-aqueous reactions

'database directory'
    'd:\min3p\database\wall2'

'define temperature'
    10.0

```

'done'

#### 4.3.4 Description of Example Input

The example input includes 9 components. The Fe(II)/Fe(III) redox couple is assumed to be at equilibrium,. The problem also includes 26 secondary aqueous species, 2 gases, and 5 minerals. The saturation indices of 2 additional minerals will be calculated. Sulfate reduction is specified to be a kinetically controlled reaction. The location of the database to be used, `wall2`, has been specified. The temperature has been specified as 10 degrees Celcius.

#### 4.3.4.1 Additional Comments

##### 4.3.4.1.1 Choosing aqueous species

It is possible to determine all the possible species for a given set of components by conducting a preliminary simulation with only the components specified. The program will generate a file (`prefix_o.psp`, where '`psp`' stands for 'possible species') containing the names of species and reactions, which can be specified. The desired species and reactions can be copied from this file into the problem-specific input file.

##### 4.3.4.1.2 Redox notes

If redox couples are specified, it is necessary to include '`o2(aq)`' as a component, since this species is used as the redox master variable.

##### 4.3.4.1.3 Adding additional species

If necessary, additional geochemical reactions can be specified in the database files (see Section 5). This is particularly useful for kinetically-controlled reactions. HOWEVER, THE DEFAULT DATABASE SHOULD NEVER BE MODIFIED. Additions or changes should be done in a copy of the default database. See Section 5 (Modifying Database, Specifying Kinetically Controlled Reactions)

## 4.4 SPATIAL DISCRETIZATION (DATA BLOCK 3)

### 4.4.1 Description of Data Block

In this data block the dimensions of the simulation are specified (1D, 2D or 3D) and the geometry of the domain is defined. The spatial discretization of the model is based on a control volume (block centered finite difference) method, and the domain must be regular (line, planer rectangle, or 3D block). However, the grid spacing can be varied in all three directions. The model uses half-cells on the boundary, which means that the grid coordinates will correspond to the actual size of the solution domain. The following diagrams show typical grid geometries for 1D, 2D and 3D scenarios.



Figure 1: Codes indicating cell spacing

## 4.4.2 Description of Input Parameters

### 4.4.2.1 'spatial discretization'

The data block for spatial discretization can be divided into sub-blocks; the first section specifies the parameters for the x-direction, while the second and third sub-blocks specify the parameters for the y- and z-directions, respectively. Within each sub-block, the first line is used to specify the number of discretization intervals or zones in that direction. If the spacing is to be uniform this value will be "1". For example, setting this value to "3" will yield three discretization zones. Within each of these zones, the grid spacing will be uniform, however the spacing may differ between zones. The discretization within each zone is specified by a series of data file entries indicating the number of cells (control volumes) within the interval followed by the spatial coordinates indicating the start and end locations for that interval (in meters).

It is necessary to specify values for all three dimensions, even for 1D- and 2D-simulations. The default values to specify are a "1" for number of zones and number of cells (control volumes) and 0.0 and 1.0 for min and max values, respectively. Orientation of your particular problem within the x-y-z coordinate system is flexible. However, when modeling variably-saturated flow, the vertical direction must be oriented in the z direction.

## 4.4.3 Example Data File Input

```
! -----
'spatial discretization'
3                               ;number of discretization intervals in x
    20                         ;number of control volumes in x
    0. 4.0                     ;xmin,xmax

    40                         ;number of control volumes in x
    4.0 10.0                   ;xmin,xmax

    40                         ;number of control volumes in x
    10.0 20.0                  ;xmin,xmax

! -----
1                               ;number of discretization intervals in y
    1                           ;number of control volumes in y
    0. 1.0                     ;ymin,ymax

! -----
1                               ;number of discretization intervals in z
```

```

20                ;number of control volumes in z
0. 4.            ;zmin,zmax

'done'

```

#### 4.4.4 Description of Example Input

The example input file is for a 2D-simulation in the x-z plane and default values have been specified for the y-axis. The total distance in the x-direction is 20 m and the total distance in the z direction is 4 m. The domain in x direction is divided into three intervals. The first interval extends from 0 to 4 m and contains 20 cells (each 0.2 m in length). The second interval extends from 4 to 10 m and contains 40 cells (each 0.15 m in length) and the third interval extends from 10 to 20 m and contains 40 cells (each 0.25 m in length). The discretization in z-direction is uniform from 0 to 4 m and contains 20 cells (each 0.2 m in length).

#### 4.4.5 Additional Notes

The decision of how many zones and what degree of discretization is required will be governed by the following factors:

Required Resolution: The spatial resolution should be capable of resolving the spatial scale of the governing physical and chemical processes.

Site specific Considerations: The coordinates specified in this section are consistent with the location of the boundaries defining the zones. If, for example, a rock with a different composition is to be specified, it is of advantage to specify this zone already when defining the spatial discretization. This allows to define exactly the areal extent of the various mineral assemblages.

Computation Limitations: The degree of discretization will be limited by the amount of memory, the computer used has available.

## 4.5 TIME STEP CONTROL (DATA BLOCK 4)

### 4.5.1 Description of Data Block

This data block controls the time steps and the final solution time. This data block is required for transient flow simulations and all reactive transport simulations. The units for the output can be specified in years, days, hours, or seconds.

The code includes an adaptive time stepping scheme, which only requires the specification of a minimum time step and a maximum time step. The minimum time step is used initially and the time step will increase to maximize efficiency. If difficulties are encountered during a simulation, the time step may decrease and, therefore, a very small minimum time step should be chosen to avoid failure of program execution. The

maximum time step may affect the accuracy of the model results. Very large time steps may lead to extensive numerical dispersion. However, many reactive transport problems, where mineral dissolution precipitation reactions control the geochemical evolution of the system allow very large time steps. Since the model is based on a fully-implicit method, there is practically no limit for the maximum time step size.

#### 4.5.2 Description of Input Parameters

##### 4.5.2.1 'time step control - global system'

Five parameters must be specified in this data block. They are tabulated below.

| Parameter           | Description  |
|---------------------|--|
| time unit           | Possible units: 'years', 'days', 'hours', or 'minutes' |
| start time          | generally set to '0.0'                                 |
| final solution time | generally the length of time of the simulation         |
| maximum time step   | Specifies the maximum # of time steps                  |
| minimum time step   | Specifies the minimum # of time steps                  |

Table 11: Summary of input parameters for data block 'time step control - global system'

The maximum and minimum time step parameters constrain the range of time steps that will be used by the code to solve the transient flow or reactive transport solution. The values selected for the minimum time step must be sufficiently small to insure that sufficient convergence occurs. This is particularly important at the beginning of the simulation. The value selected for the maximum time step may control the length of time required for a solution to be reached; increasing this value may result in a shorter run time.

#### 4.5.3 Example Data File Input

```
! -----
'time step control - global system'

'days'                ;time unit
0.0                   ;time at start of solution
1095.0                 ;final solution time
10.0                   ;maximum time step
1.0d-8                 ;minimum time step

'done'
```

#### 4.5.3.1 Description of Example Input

The example input defines a simulation time of 1095 days with a maximum time increment of 10 days and a starting time step of  $10^{-8}$  days.

#### 4.5.3.2 Additional Comments

Note that all physical and chemical input parameters such as hydraulic conductivities, diffusion coefficients, boundary fluxes, etc. are to be specified in time units of seconds independent of the time unit specified for the time step control. The chosen time unit will only affect the output times to be specified in section 4.8. This was done to allow the user to specify the simulation time and the output times on a meaningful time scale.

### 4.6 CONTROL PARAMETERS–LOCAL CHEMISTRY (DATA BLOCK 5)

#### 4.6.1 Description of Section

In this section, numerical and chemical parameters affecting the batch chemistry calculations are defined. The entire section is optional, default values are specified for all parameters in the code. Modify this section only if you are interested in enhancing the model performance, or if convergence problems occur.

#### 4.6.2 Description of Input Parameters

ULI, THIS SECTION NEEDS A FEW MORE SENTENCES OF EXPLANATION

##### 4.6.2.1 'control parameters - local geochemistry'

This data block is composed of 4 sub-blocks described below.

##### 4.6.2.2 'newton iteration settings'

In this sub-block an increment for numerical differentiation and the convergence tolerance can be specified. The increment for numerical differentiation is used to calculate numerical derivatives according to the formula

$$\frac{\partial F(C_j^c)}{\partial C_j^c} = \frac{F(C_j^c + \zeta_j) - F(C_j^c)}{\zeta_j}$$

where  $\zeta_j$  is the increment for numerical differentiation for component  $A_j^c$ , which is defined relative to the species concentration:

$$\zeta_j = \xi C_j^c$$

The value specified in the input file corresponds to  $\xi$ . The convergence tolerance defines the accuracy of the concentrations calculated during local geochemical calculations (batch, boundary or initial conditions). A solution is considered converged if the

logarithm of all concentration updates in the solution domain is smaller than the convergence tolerance  $\varepsilon$ :

$$\Delta \ln C_{j,act}^c < \varepsilon$$

#### **4.6.2.3 'output time unit'**

This sub-block can be used to specify the time unit for the output of transient evolution of the system if local geochemical calculations involve kinetic reactions.

#### **4.6.2.4 'maximum ionic strength'**

This sub-block specifies the maximum ionic strength of the solution. During convergence, it is possible that unrealistic values for ionic strength will be calculated. To avoid potential convergence problems an upper limit for the maximum ionic strength can be defined.

#### **4.6.2.5 'minimum activity for h2o'**

This sub-block is used to specify a minimum activity for water. This approach has been adopted from the geochemical equilibrium model MINTEQA2 (Allison et al., 1991).

Default values, possible settings and recommended ranges for these parameters are defined in Table 12:

| Sub-block                   | Parameter                               | Default value | Possible parameter settings                 | Recommended range     |
|-----------------------------|---|---------------|---|-----------------------|
| 'newton iteration settings' | increment for numerical differentiation | $10^{-4}$     | -   | $10^{-8}$ - $10^{-4}$ |
|                             | convergence tolerance                   | $10^{-6}$     | -   | $10^{-8}$ - $10^{-4}$ |
| 'output time unit'          | time unit                               | 'days'        | 'seconds'<br>'minutes'<br>'days'<br>'years' | -                     |
| 'maximum ionic strength'    | value for ionic strength                | 2.0           | -   | >1                    |
| 'minimum activity for h2o'  | value for activity of H <sub>2</sub> O  | 0.5           | -   | <0.75                 |

Table 12: Summary of input parameters for data block 'control parameters - local chemistry'

### 4.6.3 Example Data File Input

```

! -----
'control parameters - local geochemistry'

'newton iteration settings'
    1.d-4                ;factor for numerical differentiation
    1.d-6                ;convergence tolerance

'output time unit'
    'days'              ;time unit (local chemistry)

'maximum ionic strength'
    1.0d0                ;max. ionic strength

'minimum activity for h2o'
    0.5d0                ;min. activity for h2o

'done'

```

#### 4.6.3.1 Additional Comments

Setting the numerical parameters in the sub-block 'newton iteration settings' to values outside the recommended ranges may lead to erroneous results or convergence failure. For calculations involving solutions with high ionic strength, the user should make sure that the settings for maximum ionic strength and minimum activity for H<sub>2</sub>O do not affect the activity calculations.

## 4.7 CONTROL PARAMETERS – VARIABLY SATURATED FLOW (DATA BLOCK 6)

### 4.7.1 Description of Data Block

In this data block, numerical and control parameters affecting the flow calculations are defined. This entire section is optional, default values are specified for all parameters in the code. This section can be invoked to enhance the model performance, or if convergence problems occur.

### 4.7.2 Description of Input Parameters

#### 4.7.2.1 'control parameters - variably saturated flow'

The sub-blocks for this data block are described below, and are also summarized in Table Table 13 together with the corresponding default settings, possible parameter settings and the recommended range for the parameters.

#### 4.7.2.2 'mass balance'

If the text string 'mass balance' is included, the model will perform mass balance calculations including contributions of storage and fluxes across the domain boundary. Total system mass, mass balance contributions as change per time unit and as cumulative changes are reported in the files `prefix_o.mvs` and `prefix_o.mvc`. Mass balance errors are documented in the file `prefix_o.mve`. Additional information about the content of these files can be found in the file `prefix_o.flr`, which is created at run-time.

#### 4.7.2.3 'input units for boundary and initial conditions'

This sub-block controls the input units for the flow problem. The default unit is 'hydraulic head', as an alternative 'pressure head' can be specified. The program expects that initial and first type boundary conditions in Section 12 ('initial condition - variably saturated flow') and Section 13 ('boundary conditions - variably saturated flow') are specified in consistent units.

#### 4.7.2.4 'centered weighting'

For variably-saturated flow problems, upstream weighting of the relative permeability term leads to a more efficient solution with little loss of accuracy [Forsyth et al., 1995]. Therefore, upstream weighting is used for the relative permeability term of the unsaturated flow equation by default. If the text string 'centered weighting' is specified, centered spatial weighting will be used instead. This setting will have an effect only if partially-saturated conditions exist in the solution domain. In the case of upstream

weighting, relative permeabilities are assigned according to:

$$\begin{aligned} k_{ra,kl} &= k_{ra,k} & \text{if } h_k &\geq h_l \\ k_{ra,kl} &= k_{ra,l} & \text{if } h_l < h_k \end{aligned}$$

For centered weighting, relative permeabilities are calculated according to:

$$k_{ra,kl} = \frac{k_{ra,k} + k_{ra,l}}{2}$$

#### 4.7.2.5 'compute underrelaxation factor'

This sub-block invokes an automatic computation of under-relaxation factors for the solution of the variably-saturated flow problem [modified from Cooley, 1983 and Therrien and Sudicky, 1996]. The value below this subsection heading defines the maximum tolerable update for hydraulic head in [m]. If the computed update after application of the under-relaxation factor is larger than the maximum specified update, the update is locally set to the specified maximum update. This approach ensures that intermediate computed hydraulic head values remain in a physically reasonable range, which enhances convergence.

#### 4.7.2.6 'newton iteration settings'

This sub-block allows the specification of a number of parameters affecting the Newton-Raphson iteration loop. The first parameter identifies the increment used for the construction of the numerical derivatives:

$$\frac{\partial F(h)}{\partial h} = \frac{F(h + \xi) - F(h)}{\xi}$$

where  $h$  is hydraulic head and  $\xi$  is the increment for numerical differentiation. The following parameter identifies the maximum number of Newton iterations to be performed, before a solution is considered non-convergent. For transient flow simulations, the time step is repeated with a reduced time increment, if the number of iterations exceeds the maximum number of iterations. In the steady state case, the simulation is terminated and reported non-convergent. The next parameter specifies the convergence tolerance. A solution is considered converged if all updates for hydraulic head in the solution domain are smaller than the convergence tolerance  $\varepsilon$ :

$$\Delta h_{\max} < \varepsilon$$

The model also includes an adaptive time stepping scheme modified after Forsyth and Sammon [1986] and Therrien and Sudicky [1996], which uses the changes in aqueous phase saturation to determine the anticipated time increment. The anticipated saturation



change per time step is the last parameter specified in this subsection.

#### 4.7.2.7 'solver settings'

This sub-block allows the user to specify parameters affecting the efficiency of the sparse iterative matrix solver WATSOLV [VanderKwaak et al., 1997]. The incomplete factorization level defines the quality of the preconditioner matrix. The level of preconditioning is set to 0 by default. For difficult problems a higher level of preconditioning may be required to ensure convergence, this will also require more computer memory and increase the computational effort per solver iteration. The next parameter defines the maximum number of solver iterations. If the maximum number of solver iterations is exceeded, the solver (inner) iteration is considered non-convergent. If a transient simulation is conducted, the time step will be repeated with a decreased time increment. For a steady-state solution, the simulation will be terminated and reported non-convergent. In this case, it will be necessary to either increase the maximum number of iterations or the factorization level (improve quality of solution procedure), or to decrease the maximum allowed update (decrease difficulty of problem). The solver information level specifies how much information will be written to the file `prefix.log` and to the screen. Three different level are available:

- 0      no information
- 1      information on outer iteration (Newton iteration)
- 2      information on outer and inner iteration (Newton and solver iteration)

By default, the information level is set to 1. The next two parameters define the solver residual tolerance and the solver update tolerance. These parameters must be set to values smaller than the convergence tolerance of the Newton iteration (commonly one order of magnitude smaller).

The solver package WATSOLV (VanderKwaak et al., 1997) includes different types of ordering schemes for the matrix equations in compressed format (RCM=Reverse Cuthill McKee-ordering and natural ordering). By default, RCM-ordering is used. If the text string 'natural ordering' is included, natural ordering is used instead.

| Sub-block   | Parameter                                   | Default value    | Possible parameter settings         | Recommended range     |
|---|---|------------------|-------------------------------------|-----------------------|
| 'mass balance'                                    | -   | -                | -                                   | -                     |
| 'input units for initial and boundary conditions' | input unit                                  | 'hydraulic head' | 'hydraulic head'<br>'pressure head' | -                     |
| 'centered weighting', <sup>1)</sup>               | -   | -                | -                                   | -                     |
| 'compute underrelaxation factor', <sup>1)</sup>   | maximum update [m]                          | 10.0             | -                                   | 0.1-100.0             |
| 'newton iteration settings'                       | increment for numerical differentiation [m] | $10^{-4}$        | -                                   | $10^{-6}$ - $10^{-4}$ |
|   | maximum number of newton iterations         | 15               | -                                   | 10-30                 |
|   | convergence tolerance                       | $10^{-6}$        | -                                   | $10^{-7}$ - $10^{-4}$ |
|   | anticipated saturation change per time step | 0.1              | -                                   | 0.1-0.3               |
| 'solver settings'                                 | incomplete factorization level              | 0                | -                                   | 0-2                   |
|   | maximum number of solver iterations         | 100              | -                                   | 100-1000              |
|   | solver information level                    | 1                | 0,1,2                               | -                     |
|   | solver residual tolerance [m]               | $10^{-7}$        | -                                   | $10^{-8}$ - $10^{-5}$ |
|   | solver update tolerance [m]                 | $10^{-7}$        | -                                   | $10^{-8}$ - $10^{-5}$ |
| 'natural ordering'                                | -   | -                | -                                   | -                     |

1) only applicable under variably-saturated conditions

Table 13: Summary of input parameters for section 'control parameters - variably saturated flow'

### 4.7.3 Example Data File Input

```
! -----
'control parameters - variably saturated flow'

'mass balance'                                ;compute mass balance

'input units for boundary and initial conditions'
'hydraulic head'                             ;input unit

'centered weighting'                         ;use centered weighting

'compute underrelaxation factor'
```

```

100.0                                ;max. allowed update

'newton iteration settings'
1.0d-6                              ;increment for numerical differentiation
80                                  ;max. number of newton iterations
1.0d-4                              ;convergence tolerance
0.3                                 ;sw_star

'solver settings'
0                                    ;incomplete factorization level
100                                 ;max. number of solver iterations
0                                    ;solver information level
1.0d-7                              ;solver residual tolerance
1.0d-7                              ;solver update tolerance

'natural ordering'                  ;use natural ordering in solver

'done'

```

#### 4.7.4 Description of Example Input

In the example input section, mass balance calculations are performed, hydraulic head is used as input unit for initial and boundary conditions, centered weighting is used for the relative permeabilities. Automatic underrelaxation factor computation for variably-saturated flow is enabled with a maximum tolerable update of 100m. The increment for numerical differentiation is set to  $10^{-6}$  m, the maximum number of Newton iterations is set to 80, the convergence tolerance is set to  $10^{-4}$  m, and the anticipated change of saturation per time step is 0.3. The incomplete factorization level is set to the default value 0, the number of solver iterations is restricted to 100. The solver information level is set to 0. Values for solver residual tolerance and solver update tolerance are set to  $10^{-7}$ . The solver uses a natural ordering scheme for the preconditioner matrix.

## 4.8 CONTROL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 7)

### 4.8.1 Description of Section

In this section, numerical and control parameters affecting the reactive transport calculations are defined. The entire section is optional, default values are specified for all parameters in the code. This section may be modified to enhance the model performance, or potentially correct convergence problems.

### 4.8.2 Description of Input Parameters

The content of this section is similar to Section 6. The input parameters are described below, and are also summarized in Table 14 together with the corresponding default settings, possible parameter settings and the recommended range for the parameters.

#### 4.8.2.1 'mass balance'

If the sub-block 'mass balance' is specified, the model will perform mass balance calculations including contributions of storage, fluxes across the domain boundary and internal sources and sinks due to the specified geochemical reactions. The total system mass for aqueous phase components, minerals, gases and surface species are reported in the files `prefix_o.mas`, `prefix_o.mms`, `prefix_o.mgs` and `prefix_o.mss`. Mass balance contributions and cumulative changes are reported for each component, for each mineral phase and for all gaseous species in separate files. The file `prefix_o.flr` contains additional information on these mass balance files, the corresponding mass balance error files and their content. This file will be created for the specific problem at run-time.

#### 4.8.2.2 'spatial weighting'

Three different spatial weighting schemes can be used to describe advective transport. These options are controlled under the sub-block 'spatial weighting' and are identified by their names. The three options are 'upstream', 'van leer' and 'centered'. By default, upstream weighting will be used. In this case the concentrations for the advective mass transport term are assigned based on:

$$\begin{aligned} T_{j,kl}^a &= T_{j,k}^a & \text{if } v_{a,kl} \geq 0 \\ T_{j,kl}^a &= T_{j,l}^a & \text{if } v_{a,kl} < 0 \end{aligned}$$

where  $T_{j,kl}^a$  is the concentration at the interface of two adjacent control volumes,  $T_{j,k}^a$  and  $T_{j,l}^a$  are the concentration in the control volumes  $k$  and  $l$ , while  $v_{a,kl}$  defines the Darcy flux from control volume  $k$  to  $l$ . For centered weighting, the interfacial concentrations are defined based on:

$$T_{j,kl}^a = \frac{T_{j,k}^a + T_{j,l}^a}{2}$$

If centered weighting is used, it is necessary to obey the Peclet criterion to ensure convergence. The following requirements have to be obeyed:

$$Pe = \frac{v_{a,kl} \Delta x}{D_{a,kl}} < 2$$

where  $\Delta x$  defines the distance between the center of the two adjacent control volumes and  $D_{a,kl}$  is the effective dispersion coefficient. If the Van Leer-flux limiter is specified, the interfacial concentrations are calculated based on:

$$T_{j,kl}^a = T_{j,k}^a + \sigma(r_{kl}) \frac{T_{j,k}^a + T_{j,l}^a}{2}$$

where  $\sigma(r_{kl})$  is the Van Leer flux limiter and  $r_{kl}$  is a smoothness sensor.  $\sigma(r_{kl})$  ranges from 0 to 2 and is calculated internally (van Leer, 1994, Unger et al., 1996). The present implementation of the Van Leer flux limiter requires the Courant criteria to be obeyed:

$$Cr = \frac{v_{a,kl}\Delta t}{\Delta x} < 1$$

where  $\Delta t$  defines the time increment. Neither the Courant, nor the Peclet restrictions apply for upstream weighting, however, upstream weighting may lead to excessive numerical dispersion.

#### 4.8.2.3 'activity update settings'

The model allows several options to update activity coefficients for aqueous species. It is possible to exclude activity updates altogether by specifying 'no update' under the sub-block 'activity update settings'. By default the activity coefficients are updated after completion of each time step ('time lagged') [Lichtner, personal communication, 1997]. Alternatively, the option 'double update' can be used. In this case, the activity coefficients for all aqueous species are updated twice per Newton-iteration to maximize accuracy on the cost of performance. Comparisons have shown that differences between the option 'time lagged' and 'double update' are minimal. 'time lagged' is therefore the recommended option for calculations including activity corrections.

#### 4.8.2.4 'tortuosity correction'

If the text string below the sub-block 'tortuosity correction' is set to 'millington', the tortuosity in the aqueous and gas phase is calculated based on the relationship defined by Millington [1959]:

$$\tau = S_p^{7/3} \phi^{1/3}$$

where  $S_p$  is the phase saturation and  $\phi$  is porosity. If 'no correction' is specified, tortuosity corrections are neglected and tortuosity is set to unity.

#### 4.8.2.5 'degassing'

The sub-block 'degassing' enables degassing from the saturated zone, if the sum of the partial gas pressures exceeds the confining pressure. The value specified below the subsection header defines the degassing rate in  $\text{mol L}^{-1} \text{H}_2\text{O s}^{-1}$ .

#### 4.8.2.6 'update porosity'

The sub-block 'update porosity' enables to keep track of porosity changes due to dissolution-precipitation reactions. If this statement is enabled, porosity is calculated

based on:

$$\phi^{t+\Delta t} = \phi^t - \sum_{i=1}^{N_m} \phi_i^{t+\Delta t} - \phi_i^t$$

The porosity update will also affect the calculation of the effective diffusion coefficients. If this option is enabled, the time step should be kept sufficiently small to provide an accurate solution. This is necessary, because the update of the porosities is done explicitly after completion of a time step. Usually porosity changes are relatively slow and this simplification does not lead to significant inaccuracies.

#### 4.8.2.7 update permeability'

When the sub-block 'update permeability' is specified, the initial hydraulic conductivities are modified based on a normalized version of the Carman-Kozeny relationship. The update is of the form

$$K^{t+\Delta t} = \left[ \frac{\phi^3}{(1+\phi)^2} \right]^{t+\Delta t} \left[ \frac{(1+\phi)^2}{\phi^3} \right]^{initial} K^{initial}$$

If this option is enabled, the option 'update porosity' will be enabled automatically. As for the porosity-update, the time step needs to be kept sufficiently small, because flow and transport are treated as decoupled processes.

#### 4.8.2.8 'newton iteration settings'

This sub-block defines the parameters affecting the Newton iteration. Similar to the definitions for the geochemical batch module, the increment for numerical differentiation is used to calculate numerical derivatives according to the formula:

$$\frac{\partial F(C_j^c)}{\partial C_j^c} = \frac{F(C_j^c + \zeta_j) - F(C_j^c)}{\zeta_j}$$

where  $\zeta_j$  is the increment for numerical differentiation for component  $A_j^c$ , which is defined relative to the species concentration:

$$\zeta_j = \xi C_j^c$$

The value specified in the input file corresponds to  $\xi$ .

The following parameter specifies the anticipated number of Newton iterations, which is used internally to calculate an estimate for the time increment for the next time step. The next parameter identifies the maximum number of Newton iterations to be performed, before a solution is considered non-convergent. The time step is repeated with a reduced time increment, if the actual number of Newton iterations exceeds the maximum number of Newton iterations. The maximum number of Newton iterations must be larger than the

anticipated number of Newton iterations (commonly 3 times).

In the following the anticipated update for the primary unknowns (concentrations of components as free species) in log concentration [mol L<sup>-1</sup>] cycles is specified. Below this parameter, the maximum tolerable update (in log concentration [mol L<sup>-1</sup>] cycles) is specified. The computed update is set to the maximum tolerable update, if the computed value is larger than the maximum allowed value. This is done to ensure that the computed concentrations remain sufficiently close to the actual solution. Similar to the requirements for the maximum number of Newton iterations, the maximum tolerable update must be larger than the desired update (usually 2-3 times larger).

The convergence tolerance defines the accuracy of the concentrations calculated during the reactive transport simulation. A solution is considered converged if the logarithm of all concentration updates at each spatial discretization point in the solution domain is smaller than the convergence tolerance  $\varepsilon$ :

$$\Delta \ln C_{j,act}^c < \varepsilon$$

#### 4.8.2.9 'solver settings'

The solver package WATSOLV [VanderKwaak et al., 1997] is also used for the solution of the reactive transport problem. The settings defined in the sub-block 'solver settings' are therefore equivalent to the one for the variably-saturated flow problem and are described in the section on 'control parameters - variably saturated flow'.

#### 4.8.3 Data File Input

```
! -----
'control parameters - reactive transport'

'mass balance'

'spatial weighting'
    'upstream'                                ;spatial weighting

'activity update settings'
    'time lagged'                             ;type of activity update

'update porosity'                            ;porosity changes

'update permeability'                        ;permeability = f(porosity)

'tortuosity correction'
    'millington'                             ;Millington-Quirk tortuosity correction

'newton iteration settings'
    1.d-4                                     ;increment for numerical differentiation
    20                                       ;anticipated number of Newton iterations
    60                                       ;max. number of Newton iterations
    1.0d0                                    ;anticipated update in log cycles
    2.0d0                                    ;maximum update in log cycles
    1.d-6                                    ;convergence tolerance (global system)
```

```

'solver settings'
    0                ;incomplete factorization level
    100             ;max. number of solver iterations
    1               ;information level
    1.d-7           ;solver residual tolerance
    1.d-7           ;solver update tolerance

'natural ordering'      ;natural ordering

'degassing'
1.0e-8                ;degassing rate [mol L-1 s-1]

'done'

```

#### 4.8.4 Description of Example Input

In the example input file, mass balance calculations are performed. The code uses upstream weighting for advective transport in the aqueous phase. Activity coefficients are updated after completion of each time step. The tortuosity is corrected based on the relationship by Millington [1959]. An increment of  $10^{-4}$  (relative to the actual concentration of each primary unknown) is specified. The anticipated and maximum number of iterations in the Newton loop are 20 and 60, respectively. The anticipated update is 1 log concentration cycle, while the maximum update is locally restricted to 2 log cycles. The solution is deemed sufficiently accurate, if the magnitude of the logarithm of the concentration update is less than  $10^{-6}$ . The sparse iterative matrix solver will operate with a level 0-preconditioning, use natural ordering of the Jacobian matrix and will perform 100 solver iterations before the solution is considered non-convergent. The information level is set to 1, providing information on the Newton-loop, but not on the inner iteration. The solver residual tolerance and solver update tolerance have been specified one order of magnitude more stringent than the convergence tolerance. Degassing has been specified at a rate of  $1.0 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ .

| Subsection                              | Parameter                     | Default value | Possible parameter settings                     | Recommended range/parameter |
|---|-------------------------------|---------------|---|-----------------------------|
| 'mass balance'                          | -                             | -             | -   | -                           |
| 'spatial weighting'                     | type of weighting scheme      | 'upstream'    | 'upstream'<br>'centered'<br>'van leer'          | 'upstream'                  |
| 'activity update settings'              | type of activity update       | 'time lagged' | 'no update'<br>'time lagged'<br>'double update' | 'time lagged'               |
| 'tortuosity correction'                 | type of tortuosity correction | 'millington'  | 'millington'<br>'no correction'                 | 'millington'                |
| 'degassing'                             | degassing rate                | 0.0           | -   | system-dependent            |
| 'update porosity'                       | -                             | -             | -   | -                           |
| 'update permeability'                   | -                             | -             | -   | -                           |
| 'user-specified underrelaxation factor' | underrelaxation factor        | 1.0           | -   | 1.0                         |



|                                   |   |           |       |                       |
|-----------------------------------|---|-----------|-------|-----------------------|
| 'newton<br>iteration<br>settings' | increment for<br>numerical<br>differentiation [m]       | $10^{-4}$ | -     | $10^{-6}$ - $10^{-4}$ |
|                                   | anticipated number<br>of Newton<br>iterations           | 12        |       | 10-20                 |
|                                   | maximum number<br>of Newton<br>iterations               | 15        | -     | 20-60                 |
|                                   | anticipated<br>concentration<br>update in log<br>cycles | 0.5       | -     | 0.5-1.5               |
|                                   | maximum<br>concentration<br>update in log<br>cycles     | 1.0       | -     | 1.0-3.0               |
|                                   | convergence<br>tolerance in log<br>cycles               | $10^{-6}$ | -     | $10^{-7}$ - $10^{-4}$ |
| 'solver<br>settings'              | incomplete<br>factorization level                       | 0         | -     | 0-2                   |
|                                   | maximum number<br>of solver iterations                  | 100       | -     | 100-1000              |
|                                   | solver information<br>level                             | 1         | 0,1,2 | -                     |
|                                   | solver residual<br>tolerance [m]                        | $10^{-7}$ | -     | $10^{-8}$ - $10^{-5}$ |
|                                   | solver update<br>tolerance [m]                          | $10^{-7}$ | -     | $10^{-8}$ - $10^{-5}$ |
| 'natural<br>ordering'             | -   | -         | -     | -                     |

Table 14: Summary of input parameters for section 'control parameters - reactive transport'

## 4.9 OUTPUT CONTROL (DATA BLOCK 8)

### 4.9.1 Description of Data Block

In this data block, the output from the simulation is specified. Data can be output as a 'snapshot' at a specified time (spatial data) or as data through time at a specified location (transient data). Spatial data in 1D typically would consist of a linear plot of concentration with distance for a specified time; for a 2D simulation, the concentration data can be visualized as a 2D contour plot. Transient data typically consists of a plot of concentration with time (breakthrough curve). This section is entirely optional for all flow and reactive transport simulations and will not be considered for any batch chemistry simulations. If this section is not specified, the output will only be written at the end of the simulation.

### 4.9.2 Description of Input Parameters

#### 4.9.2.1 'output control'

This data block contains up to three sub-blocks, which are described below.

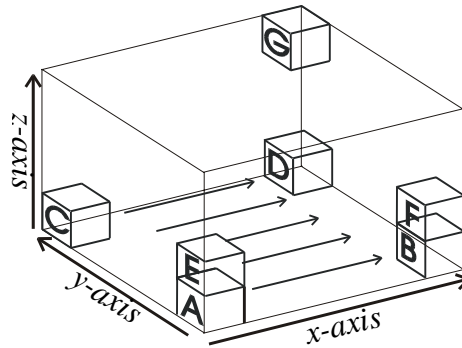
#### 4.9.2.2 'output of spatial data'

The first parameter for specifying spatial data output is the number of desired output times. This value follows the sub-block header 'output of spatial data'. The second line contains the times at which the output is desired. Only 4 output times can be specified per line, if the number of output times exceeds 4, the values for the output times have to be specified in the next line. The time units used are the same as those specified in the Section 4 ('time step control'). Spatial data is written to the files `prefix*.gs*`, as described in Section and can be post-processed with TECPLOT (reference) (Appendix describing link to TECPLOT). For example, the file `prefix_1.gst` will contain spatial data at the first (1) specified output time for total aqueous component concentrations (t).

#### 4.9.2.3 'output of transient data'

The first parameter for specifying transient data output is the number of desired output locations. This line follows the sub-block header 'output of transient data.' The second line specifies the control volume numbers of the output locations.

The control volume numbers can be calculated from the spatial discretization parameters defined in Section 'spatial discretization' (heading 4.4). Numbering of the grid is performed in x-direction first, then in y-direction and finally in z-direction.



The following parameter defines how often transient data is written to the output file (i.e.: setting this parameter to 3 means that output data will be written to the output files every third time step). Only 4 output locations can be specified per line, if the number of output locations exceeds 4, the values for the output locations have to be specified in the next line. Transient data is written to the files `prefix_*.gb*`, as described in Section 3. For example, the file `prefix_1.gbt` will contain transient data for the first (1) specified output location for total aqueous component concentrations (t).

#### 4.9.2.4 'output in terms of depth'

The spatial discretization is based on a Cartesian coordinate system, and by default the output in vertical direction is reported in terms of elevation. Optionally, the output can also be reported in terms of depth by adding the line 'output in terms of depth' to the input file. In this case the z-coordinates will be transformed prior to output based on:

$$z_i = z_{\max} - z_i$$

where  $z_{\max}$  is the maximum elevation in the solution domain (calculated internally) and  $z_i$  correspond to the elevations prior coordinate transformation and to depth values after transformation is completed.

### 4.9.3 Example Data File Input

```
! -----
'output control'

'output of spatial data'
    6                                ;number of output times (spatial data)
    1.0   2.0   5.0  10.0           ;specified output times (spatial data)
    20.0 50.0

'output of transient data'
    4                                ;number of output locations (transient
    data)                             data)
    2                                ;time steps between output (transient data)
    50  650  1250  1850             ;control volume number for transient data

'output in terms of depth'
```

'done'

#### 4.9.4 Description of Example Input

In the sample input file spatial output will be written for 6 output times. The specified output times are 1.0, 2.0, 5.0, 10.0, 20.0 and 50.0 time units. Breakthrough curves will be generated for 4 locations, which are defined by the control volume numbers 50, 650, 1250, and 1850. The output will be written every second time step and will be reported in terms of depth.

### 4.10 PHYSICAL PARAMETERS: POROUS MEDIUM (DATA BLOCK 9)

#### 4.10.1 Description of Data Block

This data block is used to specify the zones that are used to discretize a variety of physical properties across the model domain. In this section, the porosity is also specified for each zone. The zone names specified in this section are reused in other input sections to allocate physical parameters specific to variably-saturated flow or reactive transport.

#### 4.10.2 Description of Input Parameters

##### 4.10.2.1 'physical parameters - porous medium'

The first parameter that must be specified in this data block is the number of material property zones. This value is specified in the second line of this input section immediately below the heading 'physical parameters - porous medium'.

##### 4.10.2.2 'number and name of zone'

Each zone is defined by its own sub-block, which is bounded at the top by the statement 'number and name of zone' and at the bottom by the statement 'end of zone'. Each of these input blocks requires the same input sequence.

The first parameter within each block is the zone number. This value is placed immediately after the subsection header 'number and name of zone'. Property zones are numbered sequentially starting with 1 and the number of the final zone should be the same as the total number of property zones specified in the beginning of this section. The zones can be specified in any order.

The second input parameter is the name of the zone. This parameter consists of a word or



```

0.0 20.0 0.0 1.0 0.0 4.0

'end of zone'
! -----
'number and name of zone'
2
'reactive barrier'
0.50 ;porosity

'extent of zone'
8.0 12.0 0.0 1.0 0.0 3.5

'end of zone'
! -----
'number and name of zone'
3
'sand, up-gradient'
0.30 ;porosity

'extent of zone'
7.0 8.0 0.0 1.0 0.0 3.5

'end of zone'

'done'

```

#### 4.10.4 Description of Example Input

In the example file, the number of material property zones is 3. The names for the three zones in the example file are 'aquifer', 'reactive barrier' and 'sand, up-gradient'. The porosity of the different zones vary from 0.3 to 0.5. Aquifer properties are initially assigned to the entire domain and subsequently overlain by locally defined property zones. For example, the dimensions of the 2<sup>nd</sup> property zone entitled 'reactive barrier' extend from 8 to 12 m in the x-direction, 0.0-1.0m in the y-direction (default values since scenario is 2D) and 0.0 to 3.5 m in the z-direction. This zone overlays the original property zone 'aquifer'. The zone 'sand, up-gradient' allocates property zones to a sand layer located up-gradient of the reactive barrier.

## 4.11 PHYSICAL PARAMETERS-VARIABLELY SATURATED FLOW (DATA BLOCK 10)

### 4.11.1 Description of Data Block

This data block specifies physical parameters affecting the flow solution only. Parameters must be specified for each of the zones defined in Section 9 ('physical parameters - porous medium') and are identified by the names of the zones. In the case of fully-saturated conditions, the hydraulic conductivity for each spatial dimension in use needs to be specified. In the case of variably-saturated conditions, soil hydraulic function parameters (van Genuchten parameters, Woesten and van Genuchten, 1988) must also be specified. These empirical soil function parameters describe the vertical distribution of water in the unsaturated zone and provide a relationship between that water distribution and the effective hydraulic conductivity. Transient simulations require the definition of a specific storage coefficient.

## 4.11.2 Description of Input Parameters

### 4.11.2.1 `'physical parameters - porous medium'`

A sub-block is required for each material property zone defined in the previous section (`'physical parameters - porous medium'`). Each material property zone is identified by the name of the zone as specified in the previous section. The input for each material property zone is ended with the statement `'end of zone'`. Within each sub-block the following parameters are defined.

### 4.11.2.2 `'hydraulic conductivity in ?-direction'`

The hydraulic conductivity must be provided for any flow problem. Only the hydraulic conductivities for the active dimensions need to be specified. For example, a 1D-simulation in x-direction only requires the specification of `'hydraulic conductivity in x-direction'` and the corresponding hydraulic conductivity value.

### 4.11.2.3 `'specific storage coefficient'`

For transient simulations it is necessary to define a specific storage coefficient, introduced by the identifier `'specific storage coefficient'`.

### 4.11.2.4 `'soil hydraulic function parameters'`

If the simulation involves unsaturated flow, it is also necessary to define a number of soil hydraulic function parameters, including the residual saturation of the medium, the van Genuchten parameters  $\alpha$ ,  $n$ , and  $l$ , and the air entry pressure ( $p^e$ ). These parameters need to be specified below the subsection header `'soil hydraulic function parameters'`.

| Section Header  |   |                               |                                       | Required/<br>Optional   | Typical<br>Range<br>of Values |
|---|---|-------------------------------|---------------------------------------|---|-------------------------------|
| 'physical parameters - variably saturated flow'   |   |                               |                                       | required  |                               |
| Subsection*   | Parameter                               | Description                   | Required/<br>Optional                 |   |                               |
| N <sup>mz</sup> -zones  | 'hydraulic conductivity in x-direction' | $K_{xx}$ [m s <sup>-1</sup> ] | hydraulic conductivity in x-direction | only required if number of control volumes in x-direction > 1 |                               |
|   | 'hydraulic conductivity in y-direction' | $K_{yy}$ [m s <sup>-1</sup> ] | hydraulic conductivity in y-direction | only required if number of control volumes in y-direction > 1 |                               |
|   | 'hydraulic conductivity in z-direction' | $K_{zz}$ [m s <sup>-1</sup> ] | hydraulic conductivity in z-direction | only required if number of control volumes in z-direction > 1 |                               |
|   | 'specific storage coefficient'          | $S_s$ [m <sup>-1</sup> ]      | specific storage coefficient          | only required for transient flow conditions                   |                               |
|   | 'soil hydraulic function parameters'    | $S_w^r$ [-]                   | residual saturation                   | only required if not fully saturated                          |                               |
|   |   | $\alpha$ [m <sup>-1</sup> ]   | van Genuchten $\alpha$                |   |                               |
|   |   | $n$ [-]                       | van Genuchten $n$                     |   |                               |
|   |   | $l$ [-]                       | van Genuchten $l$                     |   |                               |
|   |   | $p^e$ [m]                     | air entry pressure                    |   |                               |
|   | Section Closing                         |                               |                                       |   | Required/<br>Optional         |
| 'done'  |   |                               |                                       | required  |                               |
| *All keyword headings must appear on a single line in the input file. Separation by a <Return> will result in destruction of the world as we know it. |   |                               |                                       |   |                               |

Table 15: Summary of input parameters for section 'physical parameters - variably-saturated flow'

#### 4.11.3 Example Data File Input

##### Fully Saturated Example

```
! Section 10: physical parameters - variably saturated flow
! -----
!
'physical parameters - variably saturated flow'
```



```

! -----
'aquifer'                                ;name of zone

    'hydraulic conductivity in x-direction'
        1.80d-5                                ;K_xx

    'hydraulic conductivity in z-direction'
        1.80d-6                                ;K_zz

'end of zone'

! -----
'tailings'                               ;name of zone

    'hydraulic conductivity in x-direction'
        5.00d-6                                ;K_xx

    'hydraulic conductivity in z-direction'
        1.00d-6                                ;K_zz

'end of zone'

'done'

```

### Variably Saturated Example

```

! Section 10: physical parameters - variably saturated flow
! -----
!
'physical parameters - variably saturated flow'

! -----
'silty sand'

    'hydraulic conductivity in z-direction'
        6.0d-6                                ;K_zz

    'specific storage coefficient'
        1.0d-5

    'soil hydraulic function parameters'
        0.25                                ;residual saturation
        1.50                                ;van genuchten - alpha
        2.80                                ;van genuchten - n
        0.5                                  ;expn
        0.0                                  ;air entry pressure

'end of zone'

'done'

```

#### 4.11.4 Description of Example Input

Two examples are provided for this data block. The first example is applicable for a steady state flow problem under fully-saturated conditions, while the second example includes all necessary input parameters for a transient simulation under variably-saturated conditions. The first example contains two material property zones identified by the names 'aquifer' and 'tailings'. The example is for a 2D-vertical cross-section located in the x-z-plane. Therefore the hydraulic conductivities in these two directions are specified. The hydraulic conductivity in the vertical direction for both material property zones is lower than in the horizontal direction.

The second example contains only one material property zone ('silty sand') and provides the parameters needed for a 1D-unsaturated flow problem in z-direction. In addition to the first example input section, the specific storage coefficient and the soil hydraulic function parameters are specified.

#### 4.11.5 Additional Comments

## 4.12 PHYSICAL PARAMETERS – REACTIVE TRANSPORT (DATA BLOCK 11)

### 4.12.1 Description of Data Block

This data block specifies physical parameters affecting the reactive transport solution only. Parameters must be specified for each of the zones defined in Section 9 ('physical parameters - porous medium') and are identified by the names of the zones. Parameters to be specified include diffusion coefficients and dispersivities.

### 4.12.2 Description of Input Parameters

#### 4.12.2.1 'physical parameters - porous medium'

A sub-block is required for each material property zone defined in the previous section ('physical parameters - porous medium'). Each material property zone is identified by the name of the zone as specified in the previous section. The input for each material property zone is ended with the statement 'end of zone'. An exception to this format is diffusion coefficients, which are specified only once.

#### 4.12.2.2 'diffusion coefficients'

The specification of diffusion coefficients is only necessary once in this section, because diffusion coefficients are specified as free phase diffusion coefficients, which are independent of porous medium properties. If the solution domain is fully saturated, only a free phase diffusion coefficient in water needs to be specified. This diffusion coefficient is applied to all dissolved species. Species-specific diffusion coefficients are at the present time not considered in MIN3P. The free phase diffusion coefficient should therefore represent average diffusive transport behavior for the included species. If the solution domain is partially saturated, it is necessary to also specify an average free phase diffusion coefficient in air. The input of the diffusion coefficient is initiated with the subsection header 'diffusion coefficients', followed by the values for the aqueous phase diffusion coefficient and, for the variably-saturated case, the gaseous phase diffusion coefficient.

### 4.12.2.3 'dispersivity'

Dispersivities are porous medium parameters, and need to be defined for each material property zone specified in section 9 of the input file ('physical parameters - porous medium'). The input for each zone are initiated by the name of the zone, as specified in section 9 of the input file. Dispersivities may be specified in longitudinal direction, and in transverse horizontal and transverse vertical direction. and are initiated by the headers 'longitudinal dispersivity', 'transverse horizontal dispersivity' and 'transverse vertical dispersivity', followed by the appropriate dispersivity values. Only the relevant dispersivities need to be specified. Which dispersivities are required is a function of the active dimensions (in x, y and z-direction) in the solution domain (see Table 16 for the required dispersivities). The input for each zone is ended with the statement 'end of zone'.

| Section Header  |  |  | Required/Optional                              | Typical Range of Values   |
|---|--|--|--|---|
| 'physical parameters - reactive transport'  |  |  | required for any reactive transport simulation |   |
| Subsection*   | Parameter                              | Description  | Required/Optional                              |   |
| 'diffusion coefficients'  | $D_a^0$ [ $\text{m}^2 \text{s}^{-1}$ ] | representative free phase diffusion coefficient in water | required for any reactive transport simulation |   |
|   | $D_g^0$ [ $\text{m}^2 \text{s}^{-1}$ ] | representative free phase diffusion coefficient in air   | only required if not fully-saturated           |   |
| N <sup>mz</sup> -zones  | 'longitudinal dispersivity'            | $\alpha_l$ [m]   | longitudinal dispersivity                      | only required if number of control volumes in x-direction > 1                     |
|   | 'transverse horizontal dispersivity'   | $\alpha_{th}$ [m]  | transverse horizontal dispersivity             | only required if number of control volumes in x- and y-direction > 1              |
|   | 'transverse vertical dispersivity'     | $\alpha_{tv}$ [m]  | transverse vertical dispersivity               | only required if number of control volumes in x- and z- or y- and z-direction > 1 |
| Section Closing   |  |  | Required/Optional                              |   |
| 'done'  |  |  | required                                       |   |
| *All keyword headings must appear on a single line in the input file. Separation by a <Return> will result in destruction of the world as we know it. |  |  |  |   |

Table 16: Summary of input parameters for section 'physical parameters - reactive transport'

### 4.12.3 Example Data File Input

```
! Section 11: physical parameters - reactive transport
```

```

! -----
!
'physical parameters - reactive transport'

'diffusion coefficients'
    2.0d-10                                ;aqueous phase
    2.0d-5                                 ;gaseous phase

! -----
'aquifer'                                ;name of zone

    'longitudinal dispersivity'
    0.5

    'transverse vertical dispersivity'
    0.005

'end of zone'

! -----
'tailings'                                ;name of zone

    'longitudinal dispersivity'
    0.1

    'transverse vertical dispersivity'
    0.001

'end of zone'

'done'

```

#### 4.12.4 Description of Example Input

The example input file contains two zones. Diffusion coefficients for the aqueous and gaseous phases are specified independently of these zones in the beginning of the section. The aqueous phase diffusion coefficient in the example section is  $D_a^0 = 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , and the gaseous phase diffusion coefficient is  $D_g^0 = 2 \times 10^{-5} \text{ m}^2/\text{s}^{-1}$ . The two material property zones are initiated by the names of the zones 'aquifer' and 'tailings'. (These names must be consistent with the names defined in the corresponding Section 9 of the input file 'physical parameters - porous medium'). For each of these zones dispersivities in longitudinal and transverse vertical direction are specified indicating that the section belongs to a simulation for a 2D-vertical cross section. The dispersivities for the material property zone 'aquifer' are 0.5m and 0.005m, respectively, while the dispersivities for the zone 'tailings' are 0.1 and 0.001m.

#### 4.12.5 Additional Comments

### 4.13 INITIAL CONDITION - VARIABLY SATURATED FLOW (DATA BLOCK 12)

#### 4.13.1 Description of Data block

This data block specifies the initial condition in the solution domain for the physical flow

problem. The initial condition is defined for fully saturated flow by the hydraulic head and for variably-saturated flow by the pressure head distribution. The distribution of this parameter can be discretized across the model domain. These zones do not have to coincide with the material property zones defined in section 9-11 of the input file. It is also possible to base the initial condition on an existing solution, i.e., by providing a file with a hydraulic head or pressure head value for each spatial discretization point.

#### 4.13.2 Description of Input Parameters

##### 4.13.2.1 `'initial condition - variably saturated flow'`

An sub-block is required for each material property zone defined in the previous section (`'physical parameters - porous medium'`). Each initial condition zone is identified by the name of the zone as specified in the previous section. The input for each material property zone is ended with the statement `'end of zone'`.

The zone number and a zone name are specified below the subsection header `'number and name of zone'` for each zone. The zone names may or may not be identical with the names specified for the material property zones.

##### 4.13.2.2 `'initial condition'`

The next header `'initial condition'` initiates the input of the initial condition in terms of hydraulic head or in terms of pressure head, as specified in section 6 of the input file (`'control parameters - variably saturated flow'` - if this section is not included, the input for the initial condition will be expected in terms of hydraulic head).

##### 4.13.2.3 `extent of zone'`

The specified initial condition needs to be allocated to a specific area of the solution domain below the header `'extent of zone'`. MIN3P allows the simulation of flow and reactive transport in three spatial dimensions. The following input defines the location of minimum and maximum coordinates in the x, y and z-directions for the initial condition to be allocated. If a 1D or 2D-simulation is conducted, the minimum and maximum coordinates for the excluded dimensions should be specified as 0.0 and 1.0, respectively. The input for each section is concluded with the statement `'end of zone'`. It is possible to overlay initial conditions. The input in the zone with the higher number replaces earlier input.

Alternatively, the initial condition may be read from a file, which fits a pre-specified format (the same format as defined in the `prefix_*.gsp` files, which contains the flow solution). In this case, the statement `'read initial condition from file'` needs to be included in the input section instead of the number of zones and the zone-specific input. In addition a file with the name `prefix.ivs` must be provided containing the

initial condition.

| Section Header                                |                           |  |  | Required/Optional                                 |
|---|---------------------------|--|--|---|
| 'initial condition - variably saturated flow' |                           |  |  | required for any flow simulation                  |
| 'read initial condition from file'            |                           |  |  | optional, requires file prefix.ivs                |
| $N_i$   |                           | number of zones  |  | required, if initial condition not read from file |
| Subsection                                    | Parameter                 | Description  |  | Required/Optional                                 |
| $N_i$ zones                                   | 'number and name of zone' | $i_i$  | number of zone   | required, if initial condition not read from file |
|   |                           | name   | name of zone   |   |
|   | 'initial condition'       | $h_i$ [m]<br>$p_i$ [m]   | initial hydraulic head or initial pressure head                          |   |
|   | 'extent of zone'          | $x_{min}$ [m]<br>$x_{max}$ [m]<br>$y_{min}$ [m]<br>$y_{max}$ [m]<br>$z_{min}$ [m]<br>$z_{max}$ [m] | minimum and maximum coordinates defining zone in x-, y- and z-directions |   |
|   | 'end of zone'             | -  | -  |   |
| Section Closing                               |                           |  |  | Required/Optional                                 |
| 'done'  |                           |  |  | required  |

Table 17: Summary of input parameters for section 'initial condition - variably saturated flow'

#### 4.13.3 Example Data File Input

##### Specified in Input File

```
'initial condition - variably saturated flow'
2                               ;number of zones
```

```
! -----
'number and name of zone'
1
'upper aquifer'
```

```
'initial condition'
2.0
```

```
'extent of zone'
0.0 20.0 0.0 0.0 0.0 4.0
```

```
'end of zone'
```

```
! -----
'number and name of zone'
2
'lower aquifer'
```

```
'initial condition'
```

```

1.0
'extent of zone'
0.0 20.0 0.0 0.0 0.0 2.0
'end of zone'
'done'

```

### Specified From an External File

NEED EXAMPLE!!!!!!!!!!!!!!!!!!!!!!

#### 4.13.4 Description of Example Input

In the example input section two initial condition zones are defined. The initial condition for the zone 'upper aquifer' is 2.0 m and for the zone 'lower aquifer' is 1.0 m. The units for the initial condition need to be consistent with the ones specified in Section 5 of the input file ('control parameters - variably saturated flow'). Initially, the zone 'upper aquifer' is specified for the entire solution domain, but is later partially overwritten with the initial condition specified in the zone 'lower aquifer'.

#### 4.13.5 Additional Comments

For steady state flow simulations, the initial condition is arbitrary, however, it may affect the efficiency of the solution, in particular for variably-saturated conditions. On the other hand, the initial condition for the flow problem has a direct impact for transient flow simulations and needs to be specified carefully. It may be of advantage to base a transient flow solution on an existing steady state flow solution. In this case the output of the steady state flow solution (prefix\_1.gsp) can be copied to the file prefix.ivs, which is being read as the initial condition.

## **4.14 BOUNDARY CONDITIONS - VARIABLY SATURATED FLOW (DATA BLOCK 13)**

### 4.14.1 Description of Data Block

In this data block, the flow boundary conditions for the solution domain are specified. By default, the boundaries of the solution domain are assigned as second type-Neumann boundaries with a specified flux of zero (no-flow boundary). Specific boundary conditions, which allow flow into and out of the domain can be specified.



#### 4.14.2 Description of Input Parameters

If no boundary condition are specified, the domain boundary is assumed to be impermeable. To allow flux into and out of the solution domain, it is necessary to specify boundaries that are not of this type. The options for boundary types are:

| Input Name | Boundary Type | Description             | Mathematical Expression |
|------------|---------------|-------------------------|-------------------------|
| 'first'    | Dirichlet     | Specified head boundary | $h = h_b$               |
| 'second'   | Neumann       | Specified flux boundary | $q = q_b$               |
| 'seepage'  |               | Seepage face boundary   |                         |

Table 18: Boundary conditions for flow solution

The input data for flow boundary conditions follows the format previously described for other spatially distributed properties. However, unlike for the initial condition zones or for material property zones, boundary conditions can not be overlain on each other.

##### 4.14.2.1 'boundary conditions - variably saturated flow'

The first required parameter is the number of boundary zones, which follows the section header 'boundary conditions - variably saturated flow'. Each zone is defined by a zone number and zone name following the statement 'number and name of zone'. These zones are independent of those for physical material properties or the initial condition zones, but may have the same name.

##### 4.14.2.2 'boundary type'

The statement 'boundary type' initiates the sub-block which defines what type of boundary condition is to be assigned. The actual boundary type and the numerical value of the boundary condition have to be specified immediately below this statement. The units of the numerical value for first type boundaries must coincide with those specified in Section 6 of the input file ('control parameters - variably saturated flow': 'hydraulic head' or 'pressure head', both in meters). If a second type boundary condition is assigned a boundary flux needs to be specified in units  $\text{m s}^{-1}$ . A seepage face boundary requires the specification of an estimate for the elevation of the seepage face (steady state simulation), or an initial seepage face location which should coincide with the initial condition within the domain (transient simulation).

##### 4.14.2.3 'extent of zone'

The dimensions of the boundary zone are specified below the statement 'extent of zone'. As with other spatially distributed parameters, the precise dimensions of the

boundary will be dependent on the grid spacing (See Section 3 of input file). Since the model is capable of simulating flow and reactive transport in three dimensions, the specification of the boundaries must be provided in the x, y, and z-dimensions. The coordinates are also used to specify to which boundary face the boundary condition will be applied. This is of particular importance for second type (flux) boundary conditions. For example the specification

```
'extent of zone'
0.0 0.0    0.0 1.0    0.0 10.0
```

means that the boundary condition will be applied to the y-z plane of the solution domain at  $x = 0$  covering an area from  $y_{\min} = 0$  m to  $y_{\max} = 1$  m and  $z_{\min} = 0$  m to  $z_{\max} = 10.0$  m. (Figure ??). The model formulation requires that this input structure is also obeyed for 1D- and 2D-simulations. For example, the specification of the left boundary of a 1D-simulation in x-direction would require the input:

```
'extent of zone'
0.0 0.0    0.0 1.0    0.0 1.0
```

The model can only handle boundary conditions on the surface (edges) of the solution domain. The input for each boundary zone is terminated with the statement 'end of zone'.

| Section Header                                  |                           |  | Required/Optional                    |
|---|---------------------------|--|--------------------------------------|
| 'boundary conditions - variably saturated flow' |                           |  | required for any flow simulation     |
| $N_b$   |                           | number of zones  | required for any flow simulation     |
| Subsection                                      | Parameter                 | Description  | Required/Optional                    |
| $N_b$ zones                                     | 'number and name of zone' | $i_b$<br>number of zone  | required for any flow simulation     |
|   | 'boundary type'           | name<br>type of boundary condition:<br>'first'<br>'second'<br>'seepage'  |                                      |
|   | 'extent of zone'          | $h_b$ [m]<br>$p_b$ [m]<br>$q_b$ [m s <sup>-1</sup> ]<br>hydraulic head or pressure head, if type = 'first' or 'seepage'<br>flux, if type = 'second'                            |                                      |
|   |                           | $x_{min}$ [m]<br>$x_{max}$ [m]<br>$y_{min}$ [m]<br>$y_{max}$ [m]<br>$z_{min}$ [m]<br>$z_{max}$ [m]<br>minimum and maximum coordinates defining zone in x-, y- and z-directions |                                      |
|   |                           |  |                                      |
|   |                           |  |                                      |
|   | 'end of zone'             | -  |                                      |
| Section Closing                                 |                           | Required/Optional  |                                      |
| 'done'  |                           |  | required if section header specified |

Table 19: Summary of input parameters for section 'boundary conditions - variably saturated flow'

#### 4.14.3 Example Data File Input

```
'boundary conditions - variably saturated flow'
3                                     ;number of zones

! -----
'number and name of zone'
  1
  'left boundary'

  'boundary type'
  'first' 10.0                       ;hydraulic head

  'extent of zone'
  0.0 0.0  0.0 1.0  0.0 3.5

'end of zone'

! -----
'number and name of zone'
  2
```

```

'right boundary'

'boundary type'
'first' 9.53                                ;hydraulic head (m)

'extent of zone'
30.0 30.0  0.0 1.0  0.0 3.5

'end of zone'

! -----
'number and name of zone'
3
'top boundary'

'boundary type'
'second' 1.2d-8                            ;specified flux (m s-1)

'extent of zone'
13.5 30.0  0.0 1.0  3.5 3.5

'end of zone'

'done'

```

ADD SEEPAGE FACE EXAMPLE!!!

#### 4.14.4 Description of Example Input

The example data file contains three boundary zones for a 2D-vertical cross-section located in the x-z plane with dimensions 30 m (x-direction) by 3.5 m (z-direction). The left boundary and right boundary conditions are first type boundary conditions with a value of 10.0 and 9.53 m (hydraulic head or pressure head, as specified in the Section 5 of the corresponding input file). The third boundary condition at the top of the domain is a second type boundary condition specifying an influx (recharge) of  $1.2 \times 10^{-8} \text{ m s}^{-1}$  (corresponding to 380 mm  $\text{y}^{-1}$ ). This boundary condition does not extend over the entire top boundary, but only over a zone reaching from 13.5 to 30 m.

#### 4.14.5 Additional Comments

### 4.15 INITIAL CONDITION – BATCH REACTIONS (DATA BLOCK 14)

#### 4.15.1 Description of Data Block

This data block is used to define the problem-specific chemical parameters for geochemical batch simulations. This section specifies the masses, volumes and rates of reaction for the components and reactions previously specified in Section 2 of the input file ('geochemical system'). Parameters specified in this section include the concentrations of each component present in the aqueous phase, surface site characteristics for pH dependent sorption and complexation, volume fraction of mineral

phases present and information to control the rates of mineral phase dissolution and precipitation.

Types of batch simulations that can be conducted using this data block include: speciation calculations, kinetic batch simulations, speciation and determination of exchanger or surface site composition with speciated water composition, and speciation for fixed total concentrations involving aqueous and surface complexation reactions.

For example, if you wish to calculate saturation indices for a water sample, the components and reactions of interest would be specified in data block 'geochemical system' and the amounts of the dissolved species would be specified in this data block. Alternatively, if you wished to simulate kinetically controlled dissolution of calcite, the components ( $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ , etc.) and the mineral phase calcite would be specified in the data block 'geochemical system' but the initial aqueous and solid phase concentrations would be specified in this data block. The parameters related to the rate of calcite dissolution would also be specified here.

Transient data can be generated for kinetic batch simulations. The output file (prefix\_\*.lb\*) will contain data describing the transient evolution of the geochemical composition versus time. In addition to monitoring changes with time, it is also possible to monitor changes with pH (under equilibrium conditions). These pH-sweep calculations will produce output to this file (prefix\_\*.lb\*) that can be used for the construction of pC-pH diagrams.

It is possible to carry out an unlimited number of batch problems with different geochemical assemblages in a single simulation. For example, if you had a series of water samples you wish to speciate, the specific concentrations for each sample can be specified in a separate sub-block and all the calculations would be made in a single simulation. Alternatively, can conduct a variety of separate batch problems involving different processes (e.g. kinetically controlled precipitation/dissolution, complexation, or simple speciation) in a single simulation.

## 4.15.2 Description of Input Parameters

### 4.15.2.1 `'initial condition - local geochemistry'`

The input is initiated with the data block header (`'initial condition - local geochemistry'`) followed by the number of simulations that are to be conducted. The simulation-specific input is initiated using the statement `'number and name of zone'` followed by the number and the name (up to 72 characters) identifying the simulation.

### 4.15.2.2 `'kinetic batch simulation'`

If kinetically-controlled dissolution-precipitation reactions are to be considered in the simulation, the statement `'kinetic batch simulation'` needs to be included in this input section. If a kinetic batch simulation is conducted, the transient evolution of all species involved will be reported to the output files `prefix_x.lb*`, where `x` corresponds to the number of the simulation (for content of files see file `prefix_o.fls`, generated at run-time). The geochemical composition at the end of the simulation is reported to the generic output file `prefix_o.gen`. The following parameters defines the initial time step and the final solution time for the kinetic batch simulation. The initial time step should be set to a small value and will be automatically adjusted during the course of the simulation. The magnitude of the initial time increment will be determined by the time scale of the fastest kinetic process.

### 4.15.2.3 Concentration Input

The next input block describes the unspciated water composition. An input value must be provided for each component specified in Section 2 of the input file (`'geochemical system'`) maintaining the same order as defined in Section 2.

#### 4.15.2.3.1 Input Types

Input can be provided in various ways and is controlled by the type-specification following the concentration input. Potential input units are:

- total aqueous component or total component concentrations: `'free'`
- fixed activities: `'fixed'`
- Use for charge balance: `'charge'`
- pH (only for component  $H^+$ ): `'ph'`
- pH-sweep calculations (only for component  $H^+$ ): `'ph_sweep'`
- pe, Eh (only for redox master variable and for fixed pH). `'pe'`, `'eh'`
- fixed partial pressure ( $pCO_2$  and  $pO_2$  only, if pH is fixed): `'pco2'`, `'po2'`, `'pn2'`

Total aqueous component concentrations correspond to total analytical concentrations for most components. These concentrations have to be provided in the input units specified

in Section 2 ('geochemical system') of the input file. Alternatively, a fixed activity can be specified for a specific component (also provided in the input units specified in Section 2: 'geochemical system'). For the component  $H^+$ , a fixed pH can be specified alternatively, or a pH-sweep calculation can be conducted. Additional input is required for the pH-sweep simulations. The first value in the input line is the starting-pH of the pH-sweep, while the value following the type specification 'ph\_sweep' is the final pH of the pH-sweep calculations. The last parameter in the input line defines the number of steps for the pH-sweep calculations. If a pH-sweep calculation is conducted, output for the construction of pC-pH-diagrams will be written to the output files `prefix_x.lb*`, where x corresponds to the number of the simulation (for content of files see file `prefix_o.fls`, generated at run-time). The number of steps should be set to 50 or greater to facilitate the generation of well resolved pC-pH-diagrams. A pH-sweep calculation can only be conducted for a pure equilibrium system.

Alternatively, fixed partial pressures can be specified to constrain selected components ( $O_2(aq)$ ,  $N_2(aq)$  and  $CO_3^{2-}$ ). At the present time these calculations are only accurate for a temperature of 25 °C, but may also be used as approximations for higher or lower temperatures. The specification of  $pCO_2$  also requires a fixed pH. Partial pressures are to be provided in terms of atm, independent of the input units specified in Section 2 ('geochemical system').

It is also possible to use pe or Eh to constrain the value of the standard redox master variable  $O_2(aq)$ . As for  $pCO_2$ , this specification can only be used in conjunction with a fixed pH. The calculations are only exact for 25 °C.

Alternatively, any charged component can be used to satisfy the charge balance in the equilibrated solution, provided this is physically possible. In this case it is necessary to provide an estimate for the total aqueous component concentrations.

If a component is not in the database (for example a specific organic compound), it can be added to the database `comp.dbs`. Section 5.1.1 describes the content of `comp.dbs` and provides information on how to add additional components.

#### 4.15.2.4 'sorption parameter input'

If ion exchange or surface complexation reactions are included in the simulation (as specified in section 'geochemical system'), the appropriate input parameters have to be provided for each simulation under the section header 'sorption parameter input'. The required input differs between ion-exchange and surface complexation reactions. For ion-exchange reactions, it is necessary to provide the cation exchange capacity (`cec`) and the bulk density of the porous medium (`rhobulk`). For surface complexation reactions, it is necessary to specify the name of the surface site (as previously defined in Section 2: 'geochemical system'), along with the mass, the surface area and the site density. The required input units for all ion exchange and surface complexation parameters are specified in Table 21. The model assumes by default that

the solution composition is fixed and determines the exchanger composition or the concentrations of the surface complexes based on a fixed solution composition and the specified cation exchange capacity or surface site parameters. In the case of surface complexation reactions it is also possible to use the statement `'include surface sites'` to implicitly consider the surface sites in the mass balance calculations. The essential difference between the two simulation types is that the surface reactions are excluded from initial speciation reactions by default. In this case the specified total concentrations correspond to aqueous concentrations. If surface sites are implicitly included, specified total concentrations contain sorbed and aqueous species, which implies that mass will be distributed between the aqueous phase and surface sites during speciation calculations.

#### 4.15.2.5 `'mineral input'`

If mineral phases have been specified in Section 2 (`'geochemical system'`) and the string `'kinetically-controlled dissolution-precipitation reactions'` has been included in the input section, it is necessary to specify a set of mineralogical parameters under the keyword `'mineral input'`. Two lines (6 parameters in total) are required if the update type is `'constant'` or `'twothird'`, three lines (9 parameters in total) are required for the update type `'geometric'`. A `'constant'` update type means that the mineral reactivity remains constant during the course of a simulation. This specification is most commonly used and must be applied for secondary mineral phases, i.e. mineral phases, which are not present initially. The update type-specification `'twothird'` implies that a twothird-power relationship of the form

$$k_{eff}^t = k_{eff}^0 \left( \frac{\varphi^t}{\varphi^0} \right)^{2/3}$$

is used to update the mineral reactivity (Lichtner, 1996). In this relationship,  $k_{eff}^0$  and  $\varphi^0$  define the initial effective rate constant and mineral volume fraction, respectively, while  $k_{eff}^t$  and  $\varphi^t$  define the effective rate constant and mineral volume fraction at the present solution time. The effective rate constant may be either specified directly in the input file (default option with the standard database), or it is alternatively possible to specify the reactive surface area instead. This is only meaningful, if an intrinsic rate constant for the mineral phase is specified in the database file `mineral.dbs`. Additional information on the content of the database file `mineral.dbs` and on how to add rate expressions to the database is provided in Section 0 of this document. The use of the update type `'geometric'` is not recommended, however, it is required for transport-controlled dissolution reactions described by the shrinking core model (for further information on this special topic see Theory-Section).

The first input parameter is the mineral volume fraction, i.e. the volume of bulk aquifer occupied by the specific mineral phase divided by the bulk volume of the aquifer. This quantity has been chosen, since it is convenient for reactive transport simulations. For batch simulations the volume of water is always 1 liter. The volume fraction has therefore



to be determined based on

$$\varphi_i = \frac{V_i}{1 + \sum_{k=1}^{N_m} V_k},$$

where  $\varphi_i$  is the mineral volume fraction for the input file, and  $V_i$  ( $V_k$ ) are the volumes of minerals in contact with 1L H<sub>2</sub>O. It is planned to include additional options for input units in future model versions, which are more convenient for batch simulations [mol L<sup>-1</sup> H<sub>2</sub>O or g L<sup>-1</sup> H<sub>2</sub>O]. The mineral volume [L] can be determined from the mineral weight using

$$V_i = 10^3 \frac{G_i}{\gamma_i},$$

where  $G_i$  is the mineral mass [g] and  $\gamma_i$  is the density [g cm<sup>-3</sup>] of the mineral phase and 10<sup>3</sup> is a conversion factor [cm<sup>3</sup> L<sup>-1</sup>]. The densities for common minerals are included in the database `mineral.dbs` and are summarized in the Appendix. If the mineral content is provided in moles, the conversion can be performed using:

$$V_i = 10^3 \frac{M_i GFW_i}{\gamma_i}$$

where  $M_i$  is the mineral mass in moles and  $GFW_i$  is the gram formula weight of the mineral phase [g mol<sup>-1</sup>]. The following input parameter (`minequil`) is a logical statement defining if the specific mineral phase is allowed to react in the batch simulation. If this statement is set to `.true.`, the specific mineral phase may dissolve or precipitate, otherwise the mineral phase will not participate actively in the simulation (SI's are calculated nevertheless). The last parameter in the first input line defines the `update_type`, which was introduced previously. In the second line, a minimum mineral volume fraction has to be specified. This parameter can be set to 0.0 if the update type is `'constant'`. If the update type is `'twothird'`, a value of 0.0 will prohibit the re-formation of a mineral phase, after it has been dissolved completely. It is therefore recommended to specify a small value for the minimum mineral volume fraction. This value should be chosen small enough ( $\leq 10^{-10}$ ) that the geochemical evolution is not affected notably by the mineral mass which has not been reacted. The minimum mineral volume must also be set to a small value, if the update type is `'geometric'`.

For the default database `mineral.dbs`, the next parameter defines the effective rate constant in units [mol L<sup>-1</sup> bulk s<sup>-1</sup>] for a zero order reaction. The units for higher order reactions, which depend on aqueous concentrations, are given by [mol<sup>(1-n)</sup> L<sup>n</sup> H<sub>2</sub>O L<sup>-1</sup> bulk s<sup>-1</sup>], where  $n$  defines the overall reaction order (see also Table 23). Alternatively, laboratory derived rate constants (per unit surface area) may be inserted into the database. The units for these rate constants are specified in Table 24. In this case. the reactive

surface area [ $\text{m}^2 \text{ mineral L}^{-1} \text{ bulk}$ ] needs to be specified in the problem specific datafile in place of the effective rate constant. For transport-controlled reactions, this parameter is simply a scaling factor, which includes the tortuosity of the leached layer/protective surface layer on the dissolving mineral phase. The last parameter in this row is not used and must be set to 0.0.

If a geometric update of the mineralogical parameters is used (required for transport controlled reactions), it is necessary to specify 3 additional parameters, which depend on the average grain size. The first parameter is the radius of a particle with average grain size specified in meters.. The next parameter defines the radius of the unreacted portion of the mineral [m], which must be smaller than the radius of the mineral grains specified previously in case of transport controlled reactions. (The formulation of the shrinking core model requires that the mineral particles are partially reacted initially). The last parameter defines the minimum radius for the mineral grains, which must be set to a small value.

| Section Header                           |                       |  |   | Required/Optional  |   |  |
|--|-----------------------|--|---|--|---|--|
| 'initial condition - local geochemistry' |                       |  |   | required for any batch simulation  |   |  |
| nzone                                    |                       | number of simulations                                |   | required for any batch simulation  |   |  |
| Subsection                               | Parameter             | Description  |   | Required/Optional  |   |  |
| 'number and name of zone'                | izone                 | number of simulation                                 |   | required for any batch simulation  |   |  |
|  | name                  | name of simulation                                   |   |  |   |  |
| 'kinetic batch simulation'               | delt                  | initial time step for local chemistry calculations   |   | required for any kinetic batch simulation  |   |  |
|  | tfinal                | final solution time for local chemistry calculations |   |  |   |  |
| N <sub>i</sub> zones                     | 'concentration input' | conc   | concentration input, as specified by type |  | required for all components specified in input section 'geochemical system' |  |
|  |                       | type   | 'free'                                    | specified total concentration units as specified in section 'geochemical system'                 |   |  |
|  |                       |  | 'fixed'                                   | fixed species activity, units as specified in section 'geochemical system'                       |   |  |
|  |                       |  | 'po2'                                     | fixed pO <sub>2</sub> [atm]  |   |  |
|  |                       |  | 'pn2'                                     | fixed pN <sub>2</sub> [atm]  |   |  |
|  |                       |  | 'pco2'                                    | fixed pCO <sub>2</sub> [atm]   |   |  |
|  |                       |  | 'ph'                                      | fixed pH   |   |  |
|  |                       |  | 'ph_sweep'                                | sweep over specified pH-range  |   |  |
|  |                       |  | 'pe'                                      | fixed pe   |   |  |
|  |                       |  | 'eh'                                      | fixed Eh [mV]  |   |  |
|  |                       |  | 'charge'                                  | use component to satisfy charge balance estimate in units [mol L <sup>-1</sup> H <sub>2</sub> O] |   |  |

Table 20: Summary of input parameters for section 'initial condition - local chemistry', Part 1.

|                      | Subsection                       | Parameter    | Description  | Required/Optional                                 |
|----------------------|----------------------------------|--------------|--|---|
| N <sub>i</sub> zones | 'sorption<br>parameter<br>input' | cec          | cation exchange capacity<br>[meq 100g <sup>-1</sup> soil]              | required for ion<br>exchange reactions            |
|                      |                                  | rhobulk      | dry bulk density [g cm <sup>-3</sup> ]                                 |   |
|                      |                                  | surface site | name of surface site   | required for surface<br>complexation<br>reactions |
|                      |                                  | mass         | mass of surface site<br>[g solid L <sup>-1</sup> H <sub>2</sub> O]     |   |
|                      |                                  | area         | surface area of surface site<br>[m <sup>2</sup> g <sup>-1</sup> solid] |   |
|                      |                                  | site density | site density [sites nm <sup>-2</sup> ]                                 |   |

Table 21: Summary of input parameters for section 'initial condition - local chemistry', Part 2.

| Subsection           |  | Parameter   | Description  |  | Required/Optional   |
|----------------------|--|---|--|--|---|
| N <sub>i</sub> zones | 'mineral input'  | phi   | initial mineral volume fraction<br>[m <sup>3</sup> mineral m <sup>-3</sup> bulk]   |  | required for all mineral specified in section 'geochemical system' (only if string 'kinetically-controlled dissolution-precipitation reactions' is specified) |
|                      |  | minequil  | equilibrate with mineral phases  |  |   |
|                      |  | type  | 'constant'   | no update of rate constant (surface area)                            |   |
|                      |  |   | 'twothird'   | update of rate constant (surface area) based on two-thirds power law |   |
|                      |  |   | 'geometric'  | update of rate constant (surface area) based on geometric update     |   |
|                      |  | phi_min   | minimum mineral volume fraction<br>[m <sup>3</sup> mineral m <sup>-3</sup> bulk]   |  |   |
|                      |  | k_eff   | effective rate constant<br>[mol m <sup>-3</sup> bulk s <sup>-1</sup> ]<br>(if rate constant in database is set to unity) |  |   |
|                      |  | or  | or   |  |   |
|                      |  | area  | reactive surface area<br>[m <sup>2</sup> mineral L <sup>-1</sup> bulk]<br>(if rate constant specified in database)       |  |   |
|                      |  | or  | or   |  |   |
|                      |  | factor  | scaling factor (for type 'geometric')  |  |   |
|                      |  | sat   | not used, set to 0.0   |  |   |
|                      | rad_init   | initial radius of mineral grain [m], only for type 'geometric'                      |  |  |   |
|                      | rad_surf   | initial radius of unreacted portion of mineral grain [m], only for type 'geometric' |  |  |   |
| rad_min              | minimum radius of mineral grain [m], only for type 'geometric' |   |  |  |   |
| 'end of zone'        |  | -   | -  |  |   |
| Section Closing      |  |   |  |  | Required/Optional   |
| 'done'               |  |   |  |  | required  |

Table 22: Summary of input parameters for section 'initial condition - local chemistry', Part 3.

| Reaction type  | rate expression   | units for $k_i^{m,eff}$   |
|--|---|---|
| zero order<br>default option<br>using standard<br>database | $R_i^m = -k_i^{m,eff}$<br>$R_i^m = -k_i^{m,eff} \left( 1 - \frac{IAP_i^m}{K_i^m} \right)$                     | $\text{mol L}^{-1} \text{ bulk s}^{-1}$                                       |
| $n^{\text{th}}$ order                                      | $R_i^m = -k_i^{m,eff} (T_j^a)^n$<br>$R_i^m = -k_i^{m,eff} (T_j^a)^n \left( 1 - \frac{IAP_i^m}{K_i^m} \right)$ | $\text{mol}^{1-n} \text{ L}^n \text{ H}_2\text{O L}^{-1} \text{ bulk s}^{-1}$ |
| Monod  | $R_i^m = -k_i^{m,eff} \left[ \frac{T_j^a}{K_j^{a,mo} + T_j^a} \right]$  | $\text{mol L}^{-1} \text{ bulk s}^{-1}$                                       |

Table 23: Units for effective rate constants dependent on rate expression

| Reaction type         | rate expression   | units for $k_i^m$  |
|-----------------------|---|--|
| zero order            | $R_i^m = -S_i k_i^m$<br>$R_i^m = -S_i k_i^m \left( 1 - \frac{IAP_i^m}{K_i^m} \right)$                     | $\text{mol m}^{-2} \text{ mineral s}^{-1}$                                       |
| $n^{\text{th}}$ order | $R_i^m = -S_i k_i^m (T_j^a)^n$<br>$R_i^m = -S_i k_i^m (T_j^a)^n \left( 1 - \frac{IAP_i^m}{K_i^m} \right)$ | $\text{mol}^{1-n} \text{ L}^n \text{ H}_2\text{O m}^{-2} \text{ mineral s}^{-1}$ |
| Monod                 | $R_i^m = -S_i k_i^m \left[ \frac{T_j^a}{K_j^{a,mo} + T_j^a} \right]$                                      | $\text{mol m}^{-2} \text{ mineral s}^{-1}$                                       |

Table 24: Units for rate constants dependent on rate expression (Variables NEED TO BE DEFINED!)

### 4.15.3 Example Data File Input

#### Example 1: Speciation and kinetic batch simulation

```

!
! Section 14: initial condition - local geochemistry
! -----
!
'initial condition - local geochemistry'
2                               ;number of simulations

! -----
'number and name of zone'
```

```

1
'Sierras speciation calculation'

'concentration input'
1.0d-3      'free'           ;conc,      type          - ca2+
1.0d-7      'free'           ;conc,      type          - na+
1.0d-3      'free'           ;conc,      type          - co32-
1.0d-7      'free'           ;conc,      type          - h4sio4
1.0d-7      'free'           ;conc,      type          - al3+
5.0         'ph'             ;conc,      type          - h+

'end of zone'

! -----
'number and name of zone'
2
'kinetically-controlled dissolution of calcite and albite'

'kinetic batch simulation'
1.0d-2      ;delt
1.0d0       ;tfinal

'concentration input'
1.7d-5      'free'           ;conc,      type          - ca2+
1.0d-6      'free'           ;conc,      type          - na+
2.0d-5      'free'           ;conc,      type          - co32-
1.0d-6      'free'           ;conc,      type          - h4sio4
1.0d-6      'free'           ;conc,      type          - al3+
5.0         'pH'             ;conc,      type          - h+

'mineral input'
5.0d-4      .true.          'constant' ;phi,      minequil, type - calcite
1.0d-10     1.0d-8          0.0          ;phi_min, k_eff,   sat
5.0d-1      .true.          'constant' ;phi,      minequil, type - albite
1.0d-10     1.0d-13         0.0          ;phi_min, k_eff,   sat
0.0d0       .false.         'constant' ;phi,      minequil, type - al(oh)3(am)
1.0d-10     1.0d-8          0.0          ;phi_min, k_eff,   sat
0.0d0       .false.         'constant' ;phi,      minequil, type - sio2(am)
1.0d-10     1.0d-8          0.0          ;phi_min, k_eff,   sat

'end of zone'

```

Example 2: Surface complexation

```

!
! Section 14: initial condition - local geochemistry
! -----
!
'initial condition - local geochemistry'
2                                ;number of zones

! -----
'number and name of zone'
1
'pH-sweep from 0-14, fixed total metal concentration'

'concentration input'
0.0      'ph_sweep'  14.0  50      ;conc  type  ph_final  steps  - 'h+1'
1.0d-7    'free'      ;conc  type                        - 'me+2'

'sorption parameter input'
'=soh'  1.0d0  10.0d0  6.02228d0    ;surface site, mass, area, site density

'end of zone'

! -----
'number and name of zone'
2
'ph-sweep from 0-14, fixed solution composition'

'concentration input'
0.0      'ph_sweep'  14.0  50      ;conc  type  ph_final  steps  - 'h+1'
1.00d-7   'free'      ;conc  type                        - 'me+2'

'sorption parameter input'
'=soh'  1.0d0  10.0d0  6.02228d0    ;surface site, mass, area, site density

'equilibrate with fixed solution composition'

'end of zone'

'done'

```



Example 3: Ion exchange

```

!
! Section 14: initial condition - local geochemistry
! -----
!
'initial condition - local geochemistry'
1                               ;number of zones

! -----
'number and name of zone'
1
'background chemistry - aquifer'

'concentration input'
1990.0d0    'free'              ;conc    type    - 'na+1'
100.0d0     'free'              ;conc    type    - 'k+1'
436.0d0     'free'              ;conc    type    - 'mg+2'
444.0d0     'free'              ;conc    type    - 'ca+2'
5700.0d0    'free'              ;conc    type    - 'cl-1'
7.0d0       'ph'                ;conc    type    - 'h+1'

'sorption parameter input'
10.0d0                      ;cec
1.875d0                     ;rhob

'end of zone'

'done'

```

## 4.15.4 Description of Example Input

## 4.15.5 Additional Comments

## 4.16 INITIAL CONDITION – REACTIVE TRANSPORT (DATA BLOCK 15)

## 4.16.1 Description of Section

This data block defines the initial condition for the reactive transport problem. As for the flow problem, the specification of several zones is necessary. The input structure is consistent with the one for section 'initial condition - local chemistry' with some restrictions:

- Kinetic batch simulations cannot be conducted (use batch option of model).
- pH-sweep calculations can not be conducted (use batch option of model).
- an additional input section is required defining the extent of the zone in the solution domain covered by the specified initial condition.

## 4.16.2 Description of Input Parameters

### 4.16.2.1 'initial condition - reactive transport'

The number of zones needs to be specified after the section header 'initial condition - reactive transport'. In the following, a zone number and a zone name have to be provided below the subsection header 'number and name of zone' for each zone. The zone names may or may not be identical with the names specified for the material property zones or the initial conditions for the flow problem.

The initial condition can be specified through the sections 'concentration input', 'mineral input' and 'sorption parameter input', as described in section 'initial condition - local chemistry'.

### 4.16.2.2 'extent of zone'

As for the flow problem, the specified initial condition needs to be allocated to a specific area of the solution domain below the subsection header 'extent of zone'. MIN3P allows the simulation of flow and reactive transport in three spatial dimensions. The following input defines the location of minimum and maximum coordinates in the x, y and z-directions for the initial condition to be allocated. If a 1D or 2D-simulation is conducted, the minimum and maximum coordinates for the excluded dimensions should be specified as 0.0 and 1.0, respectively. The input for each section is concluded with the statement 'end of zone'. It is possible to overlay initial conditions. The input in the zone with the higher number replaces earlier input. The input zones do not have to coincide with the material property zones or initial condition zones specified in Sections 9-12 of the input file

## 4.16.3 Example Data File Input

```
!
! Section 15: initial condition - reactive transport
! -----
!
'initial condition - reactive transport'
1                               ;number of zones

! -----
'number and name of zone'
1
'aquifer'

'concentration input'
1.7d-5      'free'              ;conc,      type          - ca2+
1.0d-6      'free'              ;conc,      type          - na+
2.0d-5      'free'              ;conc,      type          - co32-
1.0d-6      'free'              ;conc,      type          - h4sio4
1.0d-6      'free'              ;conc,      type          - al3+
5.0         'pH'                ;conc,      type          - h+

'mineral input'
5.0d-4      .true.      'constant' ;phi,      minequil, type - calcite
```

```

1.0d-10  1.0d-8    0.0      ;phi_min, k_eff,    sat
5.0d-1   .true.    'constant' ;phi,    minequil, type - albite
1.0d-10  1.0d-13   0.0      ;phi_min, k_eff,    sat
0.0d0    .false.   'constant' ;phi,    minequil, type - al(oh)3(am)
1.0d-10  1.0d-8    0.0      ;phi_min, k_eff,    sat
0.0d0    .false.   'constant' ;phi,    minequil, type - sio2(am)
1.0d-10  1.0d-8    0.0      ;phi_min, k_eff,    sat

'extent of zone'
0.0 1.0  0.0 1.0  0.0 4.0

'end of zone'

'done'

```

#### 4.16.4 Description of Example Input

#### 4.16.5 Additional Comments

### 4.17 BOUNDARY CONDITIONS - REACTIVE TRANSPORT (DATA BLOCK 16)

#### 4.17.1 Description of Section

In the last section of the problem-specific input file, the boundary conditions for the reactive transport problem need to be specified. The input is as defined in the section of 'initial condition - local chemistry' with the following exceptions:

- Kinetic batch simulations cannot be conducted (use batch option of model).
- pH-sweep calculations can not be conducted (use batch option of model).
- the subsections 'mineral input' and 'sorption parameter input' are not needed.
- an additional input section is required defining the type of boundary condition.
- an additional input section is required defining the extent of the zone in the solution domain covered by the specified initial condition.

#### 4.17.2 Description of Input Parameters

The input data for reactive transport boundary conditions follows the format previously described for other spatially distributed properties. Similar to the input for flow boundary conditions, boundary types can not be overlain on each other.

The first required parameter is the number of boundary zones, which follows the section header 'boundary conditions - variably saturated flow'.

Each zone is defined by a zone number and zone name following the statement 'number

and name of zone'. These zones are independent of those for physical material properties or the initial condition zones, but may have the same name.

Four types of boundary conditions can be specified below the subsection identifier 'boundary type':

|          |           |   |
|----------|-----------|---|
| 'first'  | Dirichlet | specified concentration   |
| 'second' | Neumann   | free exit boundary  |
| 'third'  | Cauchy    | specified mass flux   |
| 'mixed'  |           | specified aqueous mass flux,<br>fixed concentration for gaseous species on<br>dummy node outside of solution domain |

The subsection 'concentration input' is only required for first, third and mixed-type boundary conditions. For additional information on input requirements and options in this section see section 'initial condition - local chemistry'.

The dimensions of the boundary zone are specified below the statement 'extent of zone'. As with other spatially distributed parameters, the precise dimensions of the boundary will be dependent on the grid spacing (See Section 3 of input file). Since the model is capable of simulating reactive transport in three dimensions, the specification of the boundaries must be provided in the x, y, and z-dimensions. The coordinates are also used to specify to which boundary face the boundary condition will be applied. This is of particular importance for third, second and mixed type boundary conditions. For example the specification

```
'extent of zone'
0.0 0.0    0.0 1.0    0.0 10.0
```

means that the boundary condition will be applied to the y-z plane of the solution domain at  $x = 0$  covering an area from  $y_{\min} = 0$  m to  $y_{\max} = 1$  m and  $z_{\min} = 0$  m to  $z_{\max} = 10.0$  m. (Figure ??). The model formulation requires that this input structure is obeyed also for 1D- and 2D-simulations. For example, the specification of the left boundary of a 1D-simulation in x-direction would require the input:

```
'extent of zone'
0.0 0.0    0.0 1.0    0.0 1.0
```

At the present time, the model can only handle boundary conditions on the surface (edges) of the solution domain. The input for each boundary zone is terminated with the statement 'end of zone'.

#### 4.17.3 Example Data File Input

```
!
! Section 15: initial condition - reactive transport
```

```

! -----
!
'initial condition - reactive transport'
1                               ;number of zones

! -----
'number and name of zone'
1
'aquifer'

'boundary type'
'third'

'concentration input'
1.7d-5      'free'                ;conc,   type      - ca2+
1.0d-6      'free'                ;conc,   type      - na+
2.0d-5      'free'                ;conc,   type      - co32-
1.0d-6      'free'                ;conc,   type      - h4sio4
1.0d-6      'free'                ;conc,   type      - al3+
3.0         'pH'                  ;conc,   type      - h+

'extent of zone'
0.0 1.0  0.0 1.0  0.0 0.0

'end of zone'

! -----
'number and name of zone'
2
'outflow boundary'

'boundary type'
'second'

'extent of zone'
0.0 1.0  0.0 1.0  4.0 4.0

'end of zone'

'done'

```

#### 4.17.4 Description of Example Input

#### 4.17.5 Additional Comments

## 5 DATABASE

The model database is derived from the database of MINTEQA2 (Allison et al., 1991). Because MIN3P allows the simulation of open or partially open systems (in contact with the atmosphere) and the inclusion of kinetically-controlled reactions, the half-reaction approach (i.e. the use of the electron as a component and redox master variable) could not be used in MIN3P. The electron is eliminated by combining all half reactions in the MINTEQA2-database with the  $O_2(aq)/H_2O$  half reaction.

The MIN3P-database also allows the specification of kinetically-controlled intra-aqueous and dissolution-precipitation reactions. Default values for ion-exchange and surface complexation reactions are also provided and were taken from the database of PHREEQC2 (Parkhurst and Appelo, 1999).

### 5.1 COMPONENTS

#### 5.1.1 comp.dbs

The database file for the components is named `comp.dbs`. Two types of components can be specified in the database file: aqueous components and non-aqueous components (currently limited to surface sites for surface complexation reactions)

##### 5.1.1.1 aqueous components

The entry for the aqueous component  $Ba^{2+}$  is given by:

```
ba+2      2.0      5.00   .00      137.34000   0.0
```

where `ba+2` is the name of the component, `2.0` is the charge, `5.00` and `.00` are the Debye-Huckel constants  $a$  and  $b$ . `137.34000` defines the gram formula weight and `0.0` is the alkalinity factor.

##### 5.1.1.1.1 Alkalinity factor

The alkalinity factor is used to determine the alkalinity value of the water. It is defined as the proton uptake capacity of the species when titrated to the carbonate alkalinity end point. By definition, the alkalinity factor of  $CO_3^{2-}$  equals two (2).

##### 5.1.1.2 non-aqueous components

The entry for the non-aqueous component  $\equiv FeOH$  is given by:

```
=feoh      0.0      .00   .00      .00000   0.0
```

where `=feoh` is the name of the component on the surface site. The next value defines the charge of the surface species, which is defined as a component. All remaining values are arbitrary for surface complexation reactions and are set to 0.0.

### 5.1.2 Adding new components

If components are added to the database, the name of the new component must be different than the name of any existing component. If the alkalinity factor or the Debye Huckel parameters are not known, 0.00 should be specified for these values. When no Debye Huckel parameters are specified, the Davies Equation is used. All other parameters are required to allow the consideration of the new component. When adding additional components the following format must be obeyed:

Line 1: `format(a12,f4.1,4x,f5.2,f5.2,8x,f11.5,f7.2)`

Format is based on that used in MINTQA2 (e.g. a14 indicates a character string 14 characters long, f5.1 indicates a real number that contains up to four (5) digits of which one (1) is the right of the decimal place, 4x indicates four (4) blank spaces, and i3 is a three (3) digit integer)

## 5.2 COMPLEXATION REACTIONS

The database file for aqueous complexation reactions is named `complex.dbs`. As an example the database entry for the association reaction



is given by:

```
h3sio4-      6.1200   -9.8300      -1.00  4.00   .00  95.1070   .00
   2      h4sio4      1.000 h+1      -1.000
```

### 5.2.1.1 Line 1.

The first line begins with the name of the aqueous complex (h3sio4-), 6.1200 is the enthalpy change, -9.8300 is the equilibrium constant for 25°C. The following value (-1.00) defines the charge of the species, while 4.00 and .00 define the Debye Huckel constants a and b. 95.1070 is the gram formula weight of the aqueous complex, and the last value in the first input line (.00) defines the alkalinity factor for h3sio4-.

### 5.2.1.2 Line 2.

In the second line the number of components, as well as the names and stoichiometric coefficients of the components comprising the aqueous complex, are specified. In the example case, the aqueous complex consists of 2 components (h4sio4 and h+1) with stoichiometric coefficients of 1.000 and -1.000, respectively.

### 5.2.2 Adding Complexes

Additional complexes can be specified. The only requirements is that the complex can be formed from the components included in the database file `comp.dbs`. If the numerical values for the enthalpy change, the Debye-Huckel parameters or the alkalinity factor are not known, 0.00 should be specified. All other parameters must be known to allow the consideration of the aqueous complex. At the present time, the following format must be obeyed, if additional complexes are specified in the database:

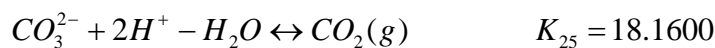
Line 1: `format(a12,2x,2f10.4,16x,3f5.2,f9.4,f7.2)`

Line 2: `format(6x,i1,3x,5(a12,1x,f7.3,1x))`

Format is based on that used in MINTEQA2 (e.g. `a14` indicates a character string 14 characters long, `f5.1` indicates a real number that contains up to four (5) digits of which one (1) is the right of the decimal place, `4x` indicates four (4) blank spaces, and `i3` is a three (3) digit integer)

## 5.3 GAS EXCHANGE REACTIONS

The database file for gas exchange reactions is named `gases.dbs`. As an example the database entry for the formation of  $\text{CO}_2(\text{g})$



is given by:

```
co2(g)      - .5300   18.1600      41.0100
   3   co3-2      1.000 h+1      2.000 h2o      -1.000
```

where `co2(g)` defines the name of the gas, `-.5300` is the enthalpy change of the reaction, `18.1600` is the equilibrium constant and `41.0100` is the gram formula weight of the gas. The input in the second line is defined analogous to the input for the aqueous complexes. The first parameter defines the number of components comprising the gas (in this case 3). In the following the names and stoichiometric coefficients of the components are specified. The three components in the example case are `co3-2`, `h+1` and `h2o` with stoichiometric coefficients of `1.000`, `2.000` and `-1.000`, respectively.

Line 1: `format(a12,2x,2f10.4,31x,f9.4/6x,i1,3x,5(a12,1x,f7.3,1x))`

## 5.4 ION EXCHANGE AND SORPTION REACTIONS

Component species involved in ion exchange and surface complexation reactions are defined in the `comp.dbs` file (see above section on component species). This section refers to the database file `sorption.dbs`, which contains secondary exchanged/adsorbed species and parameters of their formation reactions.



In the default database contains, exchange and adsorption reactions were taken from the database of PHREEQC2 (Parkhurst and Appelo, 1999).

An example for database entries for the exchange of calcium with sodium is given by:



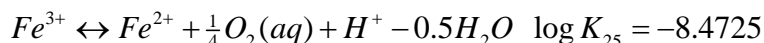
```
'ca-x(na)'      0.0000      0.7959      2.00  40.0800
2  'ca+2'  1.000  'na+1' -2.000
```

**Figure 69:** Database for exchanged and adsorbed species, *sorption.dbs*, opened where *ca-x(na)* defines the name of surface species, 0.0000 is the enthalpy change of the reaction, 0.7959 is the equilibrium constant (Gaines-Thomas), 2.00 is the electrical charge of the exchanged component (here  $\text{Ca}^{2+}$ ), and 40.0800 is the gram formula weight of the exchanged aqueous component (Ca).

The input in the second line is defined analogous to the input for the aqueous complexes and gas species. The first parameter defines the number of components (in this case 2). In the following the names and stoichiometric coefficients of the components are specified. The two components in the example case are *ca+2* and *na+1* with stoichiometric coefficients of 1.000 and -2.000, respectively. All the components should be included in the database file *comp.dbs*.

## 5.5 EQUILIBRIUM REDOX REACTIONS AND KINETICALLY-CONTROLLED INTRA-AQUEOUS REACTIONS

Equilibrium redox reactions and kinetically-controlled intra-aqueous reactions can be specified in the database file *redox.dbs*. The default database contains only equilibrium redox reactions as defined in the MINTEQA2-database (Allison et al., 1991). The database entry for the reaction:



is given by:

```
'fe+3'
4  'fe+2'      1.000  'o2(aq)'      0.250  'h+1'      1.000  'h2o'      -.500
'equilibrium' -8.4725      23.4570
```

where *fe+3* is the secondary component of the redox couple, (i.e. this component will be treated in a similar way as an aqueous complex). The string 'equilibrium' identifies the reaction as an equilibrium redox reaction. In line number 2 the number of components comprising the secondary redox species is defined, followed by the names and stoichiometric coefficients of these components. The example input has 4 components,

with the names  $\text{fe}+2$ ,  $\text{o}_2(\text{aq})$ ,  $\text{h}+1$ , and  $\text{h}_2\text{o}$  with the stoichiometric coefficients 1.000, .250, 1.000 and - .500, respectively. In the third input line the equilibrium constant for the reaction (-8.4725) and the enthalpy change (23.4570) of the reaction are specified. The fourth line requires the entry 0, which terminates the input for equilibrium reactions.

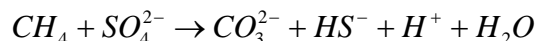
Unlike for the database files `comp.dbs`, `complex.dbs`, `gases.dbs` and `sorption.dbs`, the input in `redox.dbs` is format-free. Each line starting with ! is considered a comment line. Additional redox reaction can be entered.

It is also possible to specify irreversible, kinetically-controlled reactions in this database file. In general, the database-structure allows to describe rate expressions including fractional order terms, Monod-type terms and inhibition terms:

$$R_i^a = -k_i^a \left[ \prod_{j=1}^{N_c} (T_j^a)^{o_{ij}^{a,mo}} \prod_{j=1, K_{ij}^{a,mo} > 0}^{N_c} \left( \frac{T_j^a}{K_{ij}^{a,mo} + T_j^a} \right)^{o_{ij}^{a,mo}} \prod_{j=1, K_{ij}^{a,in} > 0}^{N_c} \frac{K_{ij}^{a,in}}{K_{ij}^{a,in} + T_j^a} \prod_{j=1, K_{ij}^{a,m,in} > 0}^{N_m} \frac{K_{ij}^{a,m,in}}{K_{ij}^{a,m,in} + \varphi_i} \right]$$

where  $R_i^m$  is the reaction rate,  $k_i^a$  is the rate constant  $T_j^a$  are the total concentrations of the aqueous components.  $K_{ij}^{a,mo}$  are the half saturation constants,  $K_{ij}^{a,in}$  are inhibition constants for aqueous components and  $K_{ij}^{a,m,in}$  are inhibition constants due to the presence of minerals.  $\varphi_i$  are the volume fractions of the inhibiting minerals.

Most commonly used are Monod-type rate expressions. For example, a reaction describing the reduction of methane by sulfate:



which is inhibited in the presence of  $\text{O}_2(\text{aq})$ ,  $\text{NO}_3^-$  and goethite is defined by the database entry:

```
!
! ch4-oxidation - sulfate reduction - Monod-kinetics
! inhibition by O2, nitrate, and goethite
!
'ch4-so4'
6 'ch4(aq)' -1.000 'so4-2' -1.000 'h2o' 1.000 'co3-2' 1.000 'hs-1' 1.000 'h+1' 1.000
'irreversible'

'hyperbolic T^a' 4
'so4-2' 1.6d-3 1.0d0
'ch4(aq)' 1.0d-5 1.0d0
'so4-2' 1.0d-10 2.0d0
'ch4(aq)' 1.0d-10 2.0d0

'inhibition T^a' 2
'o2(aq)' 3.125d-5 1.0d0
'no3-1' 1.600d-5 1.0d0

'inhibition phi^m' 1
'goethite' 1.00d-06 1.0
```

Here 'ch4-so4' is the name of the reaction (defined by the user, up to 12 characters). The second line defines the reaction stoichiometry of the reaction, starting with the number of components involved and followed by the components and the stoichiometric coefficients. The key word 'irreversible' identifies the reaction as a kinetic reaction. The number of Monod and threshold terms is specified after the key word 'hyperbolic T^a'. Threshold terms have the same form as Monod terms and may be included for numerical reasons (i.e. to turn the reaction off, if the concentrations of reacting species become very small). In each line, first the name of the component is specified, followed by the half saturation constant [mol L<sup>-1</sup>] and the exponent  $o_{ij}^{a,mo}$ . This exponent should be set to 1.0 for all Monod-type expressions, but may be set to a higher value for the threshold terms (resulting in a more rapid deactivation of the reaction when concentrations fall below the threshold limit).

The number of inhibition and toxicity terms due to the presence of aqueous components is specified after the key word 'inhibition T^a'. It is followed by the entries for these terms in the next lines. These entries consist of the names of the inhibiting components and the inhibition constants [mol L<sup>-1</sup>].

The number of inhibition and toxicity terms due to the presence of mineral phases is specified after the key word 'inhibition phi^m'. It is followed by the entries for these terms in the next lines. These entries consist of the names of the inhibiting minerals and the inhibition constants [mol L<sup>-1</sup>].

## 5.6 MINERAL DISSOLUTION-PRECIPITATION REACTIONS

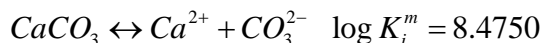
Mineral dissolution-precipitation reactions are described as kinetically-controlled reactions in MIN3P.

### 5.6.1 Surface-controlled rate expressions

The default database entry for each reaction is based on the simple rate expression:

$$R_i^m = -k_i^m S_i \left[ 1 - \left( \frac{IAP_i^m}{K_i^m} \right) \right]$$

where  $R_i^m$  is the reaction rate,  $k_i^m$  is the rate constant,  $IAP_i^m$  is the ion activity product and  $K_i^m$  is the equilibrium constant for the reaction. The default database entry for the reaction

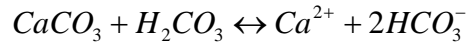


is defined by:

```
'calcite'
'surface'
100.0894 2.7100
2 'ca+2' 1.000 'co3-2' 1.000
'reversible' 8.4750 2.5850
```

where 'calcite' is the name of the mineral phase, 'surface' identifies the reaction as a surface-controlled reaction (other options are discussed below). The entries in the 3<sup>rd</sup> input line define the gram formula weight (100.0894) [g mol<sup>-1</sup>] and the density (2.7100) [g cm<sup>-3</sup>]. The first entry in the next line defines the number of components, the names of the components and the corresponding stoichiometric coefficients. The key word 'reversible' identifies the reaction as a reversible reaction (other options are discussed below). It is followed by the log $K_{25}$  of the reaction and the enthalpy change (2.5850), in [kcal mol<sup>-1</sup>].

It is also possible to use the database to include more complex dissolution-precipitation reactions. An alternative description for the dissolution of calcite follows the reaction pathways proposed by Chou et al. [1989]:



which is described by the rate expression:

$$R_i^m = -S_i \left[ k_{i1}^m \{H_2O\} + k_{i2}^m \{H_2CO_3\} + k_{i3}^m \{H^+\} \right] \left[ 1 - \frac{IAP_i^m}{K_i^m} \right]$$

The appropriate database entry is (rate data from Chou et al., 1989):

```
'calcite-ch'
'surface'
100.0894 2.710
2 'ca+2' 1.000 'co3-2' 1.000
'reversible' 8.4600 2.585

'parallel reaction pathways' 3

'pathway' 1
'log rate constant' -0.051
'activation energy' 2.000
'fractional C^c' 1
'h+1' 1.000
'end pathway'

'pathway' 2
'log rate constant' -6.187
'activation energy' 2.000
'fractional C^c' 1
'h2o' 1.000
'end pathway'

'pathway' 3
'log rate constant' -3.301
'activation energy' 2.000
'fractional C^x' 1
```

```
'h2co3aq' 1.000
'end pathway'
```

In addition to the standard database entry, an activation energy is defined (2.000, Plummer et al., 1978). The three parallel reaction pathways are included. The first and second pathways are dependent on the activity of protons and water (dependent on one component as species in solution; 'fractional C<sup>c</sup>'), while the entry for the third reaction pathway is set to 'fractional C<sup>x</sup>', because the reaction shows a dependence on the aqueous complex 'h2co3aq' (a secondary species in the MIN3P notation). The rate constants for the reactions are also provided (mass units: mol, time units: seconds) per unit surface area of the mineral (m<sup>2</sup>) with the key word 'log rate constant'. The activation energy is also specified, by means of the key word 'activation energy'.

The irreversible, pH-dependent dissolution of albite can be defined by the rate expression:

$$R_i^m = -\max \left[ S_i \left[ k_{i1}^m \{H^+\}^{0.49} + k_{i2}^m + k_{i3}^m \{OH^-\}^{-0.30} \left[ 1 - \frac{IAP_i^m}{K_i^m} \right] \right], 0 \right]$$

The appropriate database entry is:

```
'albite-ph-d'
'surface'
262.2250 2.620
5 'na+1' 1.000 'al+3' 1.000 'h4sio4' 3.000 'h+1' -4.000 'h2o' -4.000
'irreversible dissolution - log K control ' -2.5920 17.400

'parallel reaction pathways' 3

'pathway' 1
'log rate constant' -9.690
'activation energy' 13.900
'fractional Cc' 1
'h+1' 0.490
'end pathway'

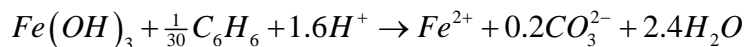
'pathway' 2
'log rate constant' -14.150
'activation energy' 13.900
'fractional Cx' 1
'oh-1' -0.300
'end pathway'

'pathway' 3
'log rate constant' -12.100
'activation energy' 13.900
'end pathway'
```

where the statement 'irreversible dissolution - log K control' is used to avoid albite precipitation under low temperature conditions. The other database entries follow the same format as was described for calcite dissolution-precipitation.

The dissolution of albite may also be described as a far from equilibrium reaction by using the string 'irreversible dissolution'.

Mineral dissolution reactions can also be described using a Monod-type formulation, similar to intra-aqueous kinetics. This is particularly useful for reductive dissolution reactions of Mn and Fe-oxides and hydroxides. The reductive dissolution of ferrihydrite in the presence of benzene for example can be described by the reaction stoichiometry:



The corresponding rate expression is:

$$R_{Fe(OH)_3-C_6H_6} = -k_{Fe(OH)_3-C_6H_6} \left[ \frac{[C_6H_6]}{K_{Fe(OH)_3-C_6H_6, C_6H_6}^s + [C_6H_6]} \right] \left[ \frac{K_{Fe(OH)_3-C_6H_6, NO_3}^i}{K_{Fe(OH)_3-C_6H_6, NO_3}^i + [NO_3^-]} \right] \left[ \frac{K_{Fe(OH)_3-C_6H_6, O_2}^i}{K_{Fe(OH)_3-C_6H_6, O_2}^i + [O_{2(aq)}]} \right]$$

The form of the rate expression is based on the assumption that the reaction is first order with respect to ferrihydrite and takes into account substrate limitation as well as inhibition of the reaction in the presence of dissolved oxygen and nitrate. This reaction can be described with the database entry:

```
'feoh3-c6h6'
'surface'
104.8692  4.3713
5  'c6h6' -0.0333  'h+1' -1.600  'co3-2' 0.200  'fe+2' 1.000  'h2o' 2.400
'irreversible dissolution'

'hyperbolic T^a' 2
'c6h6' 1.0d-3 1.000
'c6h6' 1.d-10 2.000

'inhibition T^a' 2
'o2(aq)' 3.125d-6 1.000
'no3-1' 8.000d-6 1.000

'log rate constant' 1.477d0
```

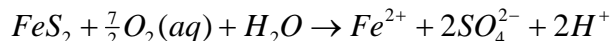
Entries for the gram formula weight of the mineral phase, the density, the number of components, the names of the components and the corresponding stoichiometric coefficients are defined as before. The reaction type is defined by the string 'irreversible dissolution'.

### 5.6.2 Diffusion-controlled rate expression

All reactions discussed up to now were surface-controlled reactions. MIN3P also allows the use of the shrinking core model to describe mineral dissolution reactions. These reactions are identified in the database file for minerals by the string 'transport' in replacement of the string 'surface'.

Due to the accumulation of alteration products on the mineral surface, the oxidation of

pyrite by dissolved oxygen may be described using the shrinking core model. The reaction stoichiometry for this reaction is:



A rate expression based on the shrinking core model can be expressed as:

$$R_i^m = -10^3 S_i \frac{r_i^p}{(r_i^p - r_i^r) r_i^r} \frac{D_{il}^m}{\nu_{il}^m} [\text{O}_2(\text{aq})]$$

In this rate expression  $10^3$  is a conversion factor [ $\text{L m}^{-3}$ ],  $S_i$  is a scaling factor including the tortuosity of the surface coating or altered rim on the mineral surface,  $r_i^p$  is the radius of the particle,  $r_i^r$  is the radius of the unreacted portion of the particle,  $D_{il}^m$  is the free phase diffusion coefficient of the primary reactant in water (in this case  $\text{O}_2(\text{aq})$ ), and  $\nu_{il}^m$  is the stoichiometric coefficient of oxygen in the reaction equation. The parameters  $S_i$ ,  $r_i^p$ , and  $r_i^r$  are specified in the problem specific input file (see Data blocks 14 or 15). The remaining parameters are not problem specific and therefore defined in the database. The database entry for the oxidative dissolution of pyrite described by the shrinking core model is:

```
'pyrite-sc'
'transport'
119.9750 5.020
5 'fe+2' 1.000 'so4-2' 2.000 'h+1' 2.000 'h2o' -1.000 'o2(aq)' -3.500
'irreversible dissolution'

'fractional C^c' 1
'o2(aq)' 1.000
'shrinking core parameters' 2.41d-9 3.500
```

Transport controlled reactions can only be described as irreversible reactions. The other database entries follow the same format as was described in the previous examples.

Additional parameters are required after the key word 'shrinking core parameters'. These are the free phase diffusion coefficient of the primary reactant in water (in  $\text{m}^2\text{s}^{-1}$ ) the stoichiometric coefficient of oxygen in the reaction equation.