Setting Up THAMES v2.5 Input

Jeffrey W. Bullard

2021-01-14 19:47:19-06:00

Contents

1 Software Requirements **1**

2 Categories of THAMES Input **1**
2.1 Thermodynamic data input 2
2.1.1 Data for system 2
2.1.2 Data for aqueous solution only 3
2.1.3 Meaning of GEMS3K the File Contents 3
2.2 Microstructure Files 4
2.2.1 Microstructure phase definitions 4
2.2.2 Rules for linking GEM phases with microstructure phases . . 7
2.2.3 Microstructure initial 3D arrangement 8
2.3 Calculation and Output Times 9

This document provides guidance on how to prepare input files for THAMES v2.5. Special attention is given to common pitfalls to avoid and some troubleshooting recommendations for fixing improper input files.

1 Software Requirements

The following software must be installed and running properly on your computer:

- GEM-Selektor 3.6.0 or 3.7.0: http://gems.web.psi.ch/GEMS3/downloads/index.html
- GEMS3K standalone library 3.4.1: http://gems.web.psi.ch/GEMS3K/downloads/index.html
- THAMES v2.5: https://github.tamu.edu/jwbullard/THAMES.git

2 Categories of THAMES Input

Throughout this document, it will be assumed that your THAMES simulation will happen in a working directory called `workdir`.

THAMES requires three categories of input files:

1. Thermodynamic data input files produced by GEM-Selektor
2. Microstructure input file and file linking microstructure phases to GEM phases

3. File to specify calculation times and microstructure output times
4. (Optional) File containing standard input to redirect to the program

Each of these will be detailed in the following sections.

2.1 Thermodynamic data input

This step requires knowledge of how to set up and run a thermodynamic calculation using GEM-Selektor.

2.1.1 Data for system

Use GEM-Selektor to construct a recipe for the system of interest, whether it be a portland cement or other geochemical system. The actual amounts of each phase or dependent component do not really matter as long as they are non-zero. A typical example for portland cement would be to choose 5.56 mol of water (`Aqua`) and 0.01 mol of dry normative air (`AtmAirNit`), and perhaps 1 g of each of the solid cement components. Be sure to place any kinetic upper constraints on phases that are known not to form in the system.

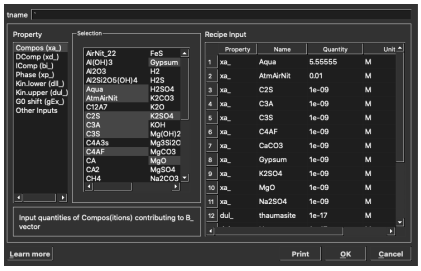

Figure 1: GEM input recipe for portland cement.

Run the recipe and accept the result in the dialog window. Confirm that the calculation has run without error and produced sensible output. When you are confident that the calculation ran smoothly, export the GEMS3K files to `workdir`:

```
Data -> Export GEMS3K files ...
```

You will need to select a root string for the output files; let us assume that the chosen root string is `portcem`. After saving, your `workdir` will now contain the following five new files:

- `portcem-dat.lst`
- `portcem-dbr-0-0000.dat`
- `portcem-dbr.lst`
- `portcem-dch.dat`
- `portcem-ipm.dat`

2.1.2 Data for aqueous solution only

Next, use GEM-Selektor to clone the system you just made in the previous step, and then edit its recipe to place an upper kinetic limit of 1×10^{-16} mol on EVERY SOLID DEPENDENT COMPONENT (DC) *except* for those you already have stated in your recipe. The purpose of this system is to enable the calculation of saturation indices of the aqueous solution with respect to the solid dependent components. The saturation indices play a central role in determining the driving force for dissolution and precipitation kinetics.

Run this cloned recipe and accept the result in the dialog window. Confirm that the calculation has run without error and produced sensible output. When you are confident that the calculation ran smoothly, export the GEMS3K files to `workdir`:

`Data -> Export GEMS3K files ...`

As before, you will need to select a root string for the output files; make this be the same as your previous root string and then add `-sol` to it. So in this case, root string is `portcem-sol`. After saving, your `workdir` will now contain another set of five new files:

- `portcem-sol-dat.lst`
- `portcem-sol-dbr-0-0000.dat`
- `portcem-sol-dbr.lst`
- `portcem-sol-dch.dat`
- `portcem-sol-ipm.dat`

Finally, open the file `portcem-sol-dat.lst` with a text editor. It should consist of one line as follows:

`-t␣"portcem-sol-dch.dat"␣"portcem-sol-ipm.dat"␣"portcem-sol-dbr-0-0000.dat"`

You must change this to make the first *two* file names be the corresponding file names of your earlier system; if you followed the instructions so far, you should just remove the `-sol` string from each of the first two files only:

`-t␣"portcem-dch.dat"␣"portcem-ipm.dat"␣"portcem-sol-dbr-0-0000.dat"`

2.1.3 Meaning of GEMS3K the File Contents

For normal usage of THAMES, one does not need to be concerned with most of the contents of the GEMS3K files. However, a few noteworthy items are as follows:

- The `-dat.lst` file contains that string that the GEMS3K library reads when performing a calculation so that it knows which other files contain the thermodynamic data it needs to run.
- The `-dch.dat` file contains the names of the independent components in the `<ICNL>` field, the names of the dependent components in the `<DCNL>` field, and the names of the phases in the `<PHNL>` field. You will need these names when

correlating microstructure phases with GEM phases. This file also contains the parameters needed to calculate the molar volumes and densities of the dependent components as a function of temperature and pressure.

- The `-dbr.dat` file contains information about the calculated state of the system you calculated using GEM Selektor, such as the activity coefficients, and phase abundances. But these will change with subsequent calculations in THAMES and so they are not of immediate concern.
- The `-ipm.dat` file contains information about the numerical parameters used in the calculations, and are not of immediate concern for using THAMES.

WARNING: With the sole exception of the modification to the `-sol-dat.lst` file already described, you must NOT modify any of the other GEMS3K input files. Doing so will likely cause the simulation to crash with a GEM error.

2.2 Microstructure Files

2.2.1 Microstructure phase definitions

The primary file for specifying microstructure phases and characteristics is given in an XML file, the schema of which is given in the `chemistry.xsd` file. We will examine the typical contents of this file for an alite cement paste.

The first several lines prescribe overall characteristics, such as the temperature, moisture conditions, and water-solids ratio.

```
<numentries>5</numentries>                <!--The number of possible phases-->
<blaine>403.2</blaine>                    <!--The Blaine fineness in cm2/kg-->
<refblaine>385.0</refblaine>              <!--Do not change this-->
<wcRatio>0.36883</wcRatio>                <!--water-solids mass ratio-->
<temperature>298.15</temperature>         <!--temperature in K-->
<reftemperature>296.15</reftemperature> <!--Do not change this-->
<saturated>0</saturated>                  <!--1 if saturated, 0 if sealed-->
```

WARNING: In the current version, the temperature should be the same as that contained in the `-dbr.dat` files. Changing the temperature will not crash the simulation but it will cause the kinetic calculations to be inconsistent with the thermodynamic calculations.

After these initial entries, one can insert an **optional** section to specify the initial concentration of solute components, which can be handy for simulating additives or adjustments to the pH. The following code shows how to specify an initial solution with a H_2SO_4 concentration of $1.0\,\mathrm{mol\,kg^{-1}}$.

```
<solution>
  <ICcomp>
  <name>H</name>       <!-- Must be an IC already defined in GEM CSD -->
  <conc>2.0</conc>     <!-- Must be given in molal units, mol/kgw -->
  </ICcomp>
  <ICcomp>
    <name>S</name>
    <conc>1.0</conc>
  </ICcomp>
```

```
    <ICcomp>
      <name>O</name>
      <conc>4.0</conc>
    </ICcomp>
</solution>
```

WARNING: Composition can be specified using **only** independent components (ICs) that are already defined in your GEM input files described earlier. One cannot specify dependent components in the current version, and the concentration units must be molal units.

The remainder of this XML file describes the various microstructure phases. The first two phases should always be `Void` and `H2O`, as shown below:

```
<!-- Do not change the first two phases here -->
<phase>
  <thamesname>Void</thamesname>
  <id>0</id>                              <!--ID used in microstructure file-->
  <interface_data>                        <!--Not used for Void phase-->
    <randomgrowth>0.0</randomgrowth>
  </interface_data>
  <porosity>0.0</porosity>                <!--Internal fraction of sat pore space-->
  <display_data>                          <!--Display rgb colors, 0 to 255-->
      <red>0.0</red>
      <green>0.0</green>
      <blue>0.0</blue>
      <gray>0.0</gray>
  </display_data>
</phase>
<phase>
  <thamesname>H2O</thamesname>
  <gemphase_data>                         <!--What GEM phase(s) is this?-->
  <gemphasename>aq_gen</gemphasename>      <!--What GEM DCs belongs to this?-->
  <gemdcname>H2O@</gemdcname>
  </gemphase_data>
  <id>1</id>                              <!--ID used in microstructure file-->
  <interface_data>                        <!--Not used for H2O phase-->
    <randomgrowth>0.0</randomgrowth>
  </interface_data>
  <porosity>1.0</porosity>                <!--Internal fraction of non-solid-->
  <display_data>                          <!--Display rgb colors, 0 to 255-->
    <red>20.0</red>
    <green>20.0</green>
    <blue>25.0</blue>
    <gray>25.0</gray>
  </display_data>
</phase>
```

Following those two microstructure phases, the other phases may have other data fields such as parameters for kinetic modeling, their relative abundance, and perhaps multiple GEM phases. An example for a dissolving portland cement component is given below:

```
<phase>
  <thamesname>C3S</thamesname>
  <gemphase_data>
  <gemphasename>Alite</gemphasename>
  <gemdcname>C3S</gemdcname>
  </gemphase_data>
  <id>2</id>                              <!--ID used in microstructure file-->
  <interface_data>
    <randomgrowth>0.0</randomgrowth>      <!--Zero means no randomness-->
    <affinity>
```

```
      <affinityphaseid>2</affinityphaseid> <!--Phase interaction with this phase-->
      <affinityvalue>1</affinityvalue>     <!--More positive means more attraction,
                                               can be negative for repulsion-->
    </affinity>
  </interface_data>
  <porosity>0.0</porosity>                 <!--Internal fraction of non-solid-->
  <impurity_data>                          <!--Impurity data in mol frac-->
    <k2ocoeff>0.00087</k2ocoeff>                <!--K2O-->
    <na2ocoeff>0.0</na2ocoeff>                  <!--Na2O-->
    <mgocoeff>0.00861</mgocoeff>                <!--MgO-->
    <so3coeff>0.007942</so3coeff>               <!--SO3-->
  </impurity_data>
  <kinetic_data>
    <type>kinetic</type>                   <!--This phase obeys kinetic model-->
    <scaledmass>100.0</scaledmass>         <!--Mass percentage on total solids basis-->
    <k1>1.5</k1>                           <!--Kinetic model parameters-->
    <k2>0.05</k2>
    <k3>1.1</k3>
    <n1>0.7</n1>
    <n3>3.3</n3>
    <Ea>41570.0</Ea>                       <!--Apparent activation energy-->
    <critdoh>2.0</critdoh>                 <!--Another kinetic model parameter-->
  </kinetic_data>
  <display_data>
    <red>162.0</red>                       <!--Display rgb values, 0 to 255-->
    <green>117.0</green>
    <blue>95.0</blue>
    <gray>220.0</gray>
  </display_data>
</phase>
```

NOTE: The <id>values MUST be in order, starting with zero for void and one for water, and then proceeding without skipping any numbers.

An example of a phase that is controlled by thermodynamics rather than kinetics is C–S–H:

```
<phase>
  <thamesname>CSH</thamesname>
  <gemphase_data>
  <gemphasename>CSHQ</gemphasename>         <!--GEM phase(s) linked to this-->
  <gemdcname>CSHQ-JenD</gemdcname>          <!--GEM DC(s) linked to gemphasename-->
  <gemdcname>CSHQ-JenH</gemdcname>
  <gemdcname>CSHQ-TobD</gemdcname>
  <gemdcname>CSHQ-TobH</gemdcname>
  <gemdcname>KSiOH</gemdcname>
  <gemdcname>NaSiOH</gemdcname>
  </gemphase_data>
  <id>4</id>                               <!--ID used in microstructure file-->
  <interface_data>
    <randomgrowth>0.6</randomgrowth>       <!--Grows in a fairly random manner-->
    <affinity>
      <affinityphaseid>2</affinityphaseid> <!--Same as one of the templates above-->
      <affinityvalue>4</affinityvalue>     <!--More positive means more attraction,
                                               can be negative for repulsion-->
    </affinity>
    <affinity>
      <affinityphaseid>3</affinityphaseid>
      <affinityvalue>1</affinityvalue>
    </affinity>
    <affinity>
      <affinityphaseid>4</affinityphaseid>
      <affinityvalue>1</affinityvalue>
    </affinity>
  </interface_data>
  <porosity>0.27</porosity>
```

```
  <kinetic_data>
    <type>thermo</type>                    <!--This phase is governed by thermo-->
    <scaledmass>0.0</scaledmass>           <!--No kinetic data needed for thermo phase-->
  </kinetic_data>
  <display_data>                           <!--Display rgb values, 0 to 255-->
    <red>245.0</red>
    <green>222.0</green>
    <blue>179.0</blue>
    <gray>159.0</gray>
  </display_data>
</phase>
```

NOTE: Every solid phase MUST have an <affinity> for itself, with an <affinityvalue> greater than zero.

Finally, a phase called DAMAGE must ALWAYS be present, and should be the final phase in the list.

```
<phase>
  <thamesname>DAMAGE</thamesname>
  <id>5</id>
  <interface_data>
    <randomgrowth>0.0</randomgrowth>
  </interface_data>
  <porosity>1.0</porosity>
  <display_data>
    <red>255.0</red>
    <green>0.0</green>
    <blue>255.0</blue>
    <gray>255.0</gray>
  </display_data>
</phase>
```

2.2.2 Rules for linking GEM phases with microstructure phases

A microstructure phase can be associated with zero, one, or multiple GEM phases; the user must decide which GEM phase or phases should be associated with a given microstructure phase. In some cases the choice will be obvious, such as identifying aq_gen as the saturated pore liquid in the microstructure. But in other cases it may be useful or efficient to group two or more GEM phases into a single microstructure phase. One example might be to collect all of the GEM phases associated with carboaluminates, of which there are many, into a single microstructure phase called AFm_c or something like that, as shown in this example:

```
<phase>
  <thamesname>MONOSULPH</thamesname>
  <gemphase_data>
      <gemphasename>C4AsH105</gemphasename>
      <gemdcname>monosulphate10.5</gemdcname>
  </gemphase_data>
  <gemphase_data>
      <gemphasename>C4AsH12</gemphasename>
      <gemdcname>monosulphate12</gemdcname>
  </gemphase_data>
  <gemphase_data>
      <gemphasename>C4AsH14</gemphasename>
      <gemdcname>monosulphate14</gemdcname>
  </gemphase_data>
  <gemphase_data>
      <gemphasename>C4AsH9</gemphasename>
```

```
        <gemdcname>monosulphate9</gemdcname>
    </gemphase_data>
    <gemphase_data>
        <gemphasename>monosulph-AlFe</gemphasename>
        <gemdcname>monosulphate1205</gemdcname>
        <gemdcname>Fe-monosulph05</gemdcname>
    </gemphase_data>
    <id>13</id>
    <interface_data>
      <randomgrowth>0.6</randomgrowth>
```

etc.

```
    </phase>
```

Whatever choices are made, both the GEM phase name and the names of all the DC components for that phase must be placed within <gemphase_data> field, and there must be one of these fields for each GEM phase that you wish to link to the microstructure phase. In addition, the gemphasename must exactly match one of the <PHNL> entries in the -dch.dat file, and *all* of the DCs associated with that phase must immediately follow that phase as shown in this example. Determine which GEM DCs are associated with a given phase by consulting the <nDCinPH> field of the -dch.dat file.

To illustrate, Figure 2 shows a portion of a real -dch.dat file. In the figure, there are *nine* phases listed in the <PHNL> field and 26 DCs listed in the <DCNL> field. The numbers in the <nDCinPH> field relate the two. Notice that there are *nine* numbers in <nDCinPH>, one for each phase. The ordering of the numbers is the same as the ordering of phase names in the <PHNL> field. So there are 13 DCs in the first phase, which is <aq_gen>. In addition, those 13 DCs are the *first* 13 DCs in the <DCNL> list. Moving on, we see that there are three DCs in the next phase, which is gas_gen, and those three DCs are the next three after the first 13 in the <DCNL> list, namely 'H2', 'O2', and 'H2O' (the last being the water vapor molecule, not liquid water which is H2O@[1]

2.2.3 Microstructure initial 3D arrangement

The microstructure representation is a digitized 3D image with X_Size voxels in the x direction, Y_Size in the y direction, and Z_Size in the z direction. Each voxel is a physical dimension of Image_Resolution in micrometer units. This is a normal ASCII text file. The first few lines of an example microstructure are given below.

```
Version: 5.0
X_Size: 100
Y_Size: 100
Z_Size: 100
Image_Resolution: 1.0
1
1
1
```

[1] In GEMS, the '@' symbol is reserved to designate a zero-charge liquid solvent or a zero-charge dissolved component. Gas molecules do not have this symbol even though they also have zero charge.

```
## (6) Dependent Components and their codes
# DCNL: Name list of Dependent Components (<=16 characters per name) [nDC]
<DCNL>
'Ca+2' 'CaOH+' 'Ca(HSiO3)+' 'CaSiO3@' 'HSiO3-' 'Si4O10-4' 'SiO2@' 'SiO3-2' 'H2@' 'O2@' 'OH-' 'H+'
'H2O@' 'H2' 'O2' 'H2O' 'CSHQ-JenD' 'CSHQ-JenH' 'CSHQ-TobD' 'CSHQ-TobH' 'C2S' 'C3S' 'Lim'
'Portlandite' 'Qtz' 'Amor-S1'
# ccDC: Class codes of DCs (Dependent Components) [nDC]
<ccDC>
'S' 'S' 'S' 'S' 'S' 'S' 'S' 'S' 'S' 'S' 'S' 'T' 'W' 'G' 'G' 'G' 'I' 'I' 'I' 'I' 'O' 'O' 'O' 'O' 'O'
'O'

# DCmm: Molar masses of DCs, kg/mol [nDC]
<DCmm>
0.04007799911149902 0.05708534920215561 0.117169650197029 0.116161700248718 0.0770916510820389 0.
2723360042572002 0.06008430099487 3 0.076083701133728 0.0020158998966217 0.03199880027771 0.
01700735008716508 0.0010079499483 1085 0.018015300035476 7 0.0020158998966217 0.03199880027771 0.
018015300035476 7 0.16921252442741 0.17386048006892 0.11982140754 3999 0.12449405313062 7 0.
17223909950256 3 0.228316498756409 0.05607739925384 52 0.07409269928932 19 0.06008430099487 3 0.
060084300994873

## (7) Phases and their codes
# PHNL: List of Phase names (<=16 characters per name) [nPH]
<PHNL>
'aq_gen' 'gas_gen' 'CSHQ' 'Belite' 'Alite' 'lime' 'Portlandite' 'Quartz' 'Silica-amorph'
# ccPH: Codes of phase aggregate state [nPH]
<ccPH>
'a' 'g' 's' 's' 's' 's' 's' 's' 's'
# nDCinPH: Number of DCs included in each phase [nPH]
<nDCinPH>
13 3 4 1 1 1 1 1 1
```

Figure 2: Portion of a DCH input file showing the definitions of GEM phases and DCs.

```
2
1
2
1
```

Note that the `Version` descriptor is not currently used. After the five-line header to this file, each line contains a single integer corresponding to the ID of one of the microstructure phases (not the GEM phases). The rows have a `z-y-x` nesting convention, by the first voxel is $(0, 0, 0)$, the x coordinates vary most quickly and the z coordinates vary most slowly.

One way to generate such a file is to create a virtual 3D microstructure using VCCTL, which produces a `.img` file in much the same format as just shown. However, the VCCTL phase ID numbers (Table 1) are different than the ones required by THAMES. Therefore, one must replace the VCCTL ID numbers with the corresponding THAMES microstructure id numbers. A C program called `vcctl2thames` has been provided to assist with this, but the program may need to be edited as needed to be consistent with the THAMES microstructure definition file (`chemistry.xml`).

2.3 Calculation and Output Times

The file for specifying calculation times and output times is an XML file, the schema of which is given in the `parameters.xsd` file. Each calculation time is specified (in days) with a line like this:

```
<calctime>0.001331</calctime>
```

Generally, it is a good idea to have a lot of calculation times using closely spaced time intervals, especially at early times. This is needed to prevent the kinetic changes

Table 1: VCCTL 9.5 phase identification numbers

Phase	ID	Phase	ID	Phase	ID
Water	0	Gypsum	7	$Ca(OH)_2$	19
Void	55	Bassanite (Hemihydrate)	8	C–S–H	20
Alite	1	Anhydrite ($CaSO_4$)	9	C_3AH_6	21
Belite	2	Silica Fume	10	Ettringite	22
C_3A	3	Inert	11	$Fe(OH)_3$	25
C_4AF	4	Silica glass	16	Pozzolanic C–S–H	26
K_2SO_4	5	Monosulfate	24	Friedel salt	29
Na_2SO_4	6	Monocarboaluminate	34	$CaCl_2$	28
$CaCO_3$	33	Strätlingite	30	Brucite	35

during any time interval from being so large that the thermodynamic equilibrium calculations cannot converge.

After all the calculation times have been specified, the user can specify any number of simulation times (in days) at which to output a 3D microstructure image. The syntax for this is

```
<outtime>28.0</outtime>
```