Commented run of THERIAK

This example uses the database JUN92.bs. The calculation is done at 600 ^{o}C and 4000 Bar, for a bulk composition corresponding to 10 paragonite and 10 muscovite, with excess H_2O and SiO_2.
This is defined in the dat-file (containing P, T and bulk composition) with two lines. The dat-file us usually called THERIN or therin.txt. Edit this file, so that the first two lines (not counting the comment lines beginning with "!") are as follows:

```
600     4000
1   SI(160)AL(60)NA(10)K(10)H(100)O(?)     *
```

Start the program Theriak: In a UNIX shell or in the Mac OsX Terminal or in the "start.bat" batch window on a PC you type the command "theriak" and enter Return.
In the following, the framed text (font courier) is the screen output of the program. The user input is bold.

theriak
```
Program THERIAK, Version (dd.mm.yy) 01.08.09 (MacOsX, gfortran)
 =============================================================

 "Computation of equilibrium assemblages at given PT"


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 ==============================================================================
```

This is the prolog of the program. Depending on the version used and the platform, the first few lines may look slightly different or may be missing. Some lines may have been inserted by the person istalling the program as a control, that the correct directories were chosen. (or to add their own name as author).
The title includes the version number, the operating system and the compiler used to install the software.

```
 --------------
 initialization
 --------------
 Initialization-file:   /user_capi/capi/gnugnu/DominoTheriak111207/theriak.ini
 Program's directory:   /user_capi/capi/gnugnu/DominoTheriak111207/
 Working directory:     /user_capi/capi/gnugnu/tests_and_examples/pixelmapsandH2Oact/

 Run: 16.06.2009 - 10:32:51
```

Program's directory: Depending on the installation and how you invoke the program, this is the absolute or relative path of the directory containing the running program.

Working directory: Current directory from where you typed the command. (**However**: if this directory does not contain a dat-file (containing P, T and bulk composition) the working directory will be set equal to the program's directory.

In order to run, the program needs the initialization file "theriak.ini". (This file contains the personal settings, like calculation parameters and the file names of input and output). If "theriak.ini" is found in the working directory, this will be used. If not, the one in the program's directory is used. In neither is found, the program stops.

The run is identified by the date and time.

```
 -------------------
 database definition
 -------------------
 Enter [ "?" | CR | "files" | database filename ] < >?
```

At this point the program asks for a database file. If a log-file (a file containing most interactive input from a previous run) exists, the last used database filename is proposed, which you can accept by entering an empty line (CR). Else you type the file name of the database, which must be located in the working directory.

The keyword "files" will provide you with the information on file names as defined in "theriak.ini"

JUN92.bs

```
database for this run: JUN92.bs


 Input from file THERIN
 ----------------------
 T =  600.00 C    P =   4000.00 Bar
 1   SI(160)AL(60)NA(10)K(10)H(100)O(?)     *
```

Summary of the input. The last two lines are the information found in the dat-file (containing P, T and bulk composition. Its name is defined in "theriak.ini". In this case it is "THERIN"). This file must be located in your working directory.

(**Note** that the first character of the bulk composition line is "1". This means, that we will get a "long output" with information on bulk composition, considered phases, solution phases, compositions of stable phases and activities of all phases. A "0" at the beginning of the line will suppress these paragraphs.)

```
 --------------------------
 define type of calculations
 --------------------------
 Enter [ "?" | CR | "no" | "bin" | "loop" | filename ] < >?
```

At this point you have different options. The simplest is "no", which will calculate a single equilibrium with the P, T and bulk composition defined in the dat-file. For more information enter "?".
In this example we use "no", and the calculation starts.

no

```
SI(160)AL(60)NA(10)K(10)H(100)O(?)     *

 TEST = 1.0000E-09        LO1MAX = 300         EQUALX = 1.0000E-02    DELXMIN = 1.0000E-09
 DELXSCAN = 1.0000E+00    DELXSTAR = 1.0000E-04  STEPSTAR =  25        STEPMAX =  25         GCMAX =  500
```

These are the calculation parameters (Beginners just ignore them)

TEST ΔG Testvalue to stop iterations.
LO1MAX   Maximum number of iterations.
EQUALX   Two phases of the same solution are considered equal if Δxi < EQUALX.
DELXMIN   smallest possible stepsize = precision for calculating xi's in a non-ideal solution.
DELXSCAN   Grid width for scanning non-ideal solution phases for initial solution.
DELXSTAR   initial stepsize.
STEPSTAR   Maximum number of steps, if initial solution results from a scan.
STEPMAX   Maximum number of steps if initial solution is a previous minimum.
GCMAX   Maximum number of G-function calls per step. (= maximum m in stepsize procedure)

```
 P =  4000.00 bar    P(Gas) =  4000.00 bar    T =  600.00 C   =   873.15 K
```

P   Pressure
P(Gas)   Gases may have a different pressure. (see input description)
T   Temperature in C and K

```
 ------------
 composition:      N            N           mol%
 ------------

    1  O       470.000000   4.70000E+02    58.024691
    2  AL       60.000000   6.00000E+01     7.407407
    3  H       100.000000   1.00000E+02    12.345679
    4  K        10.000000   1.00000E+01     1.234568
    5  NA       10.000000   1.00000E+01     1.234568
    6  SI      160.000000   1.60000E+02    19.753086
    7  E         0.000000   0.00000E+00     0.000000
```

Bulk omposition for which an equilibrium assemblage will be calculated.
N   number of moles of a component (usually elements)
mol%   Calculated to a sum of 100. (not very useful)

Note: E is an elementary charge, and used with aqueous solutions. Its bulk is always zero (charge-balance) and has absolutely no influence on any non-aqueous calculations. Ignore it.

```
------------------
considered phases:
------------------
                                 G       O     AL    H     K     NA    SI    E

    1  "O"            :        0.00    1.00    -     -     -     -     -     -
    2  "AL"           :        0.00     -    1.00    -     -     -     -     -
    3  "H"            :        0.00     -     -    1.00    -     -     -     -
    4  "K"            :        0.00     -     -     -    1.00    -     -     -
    5  "NA"           :        0.00     -     -     -     -    1.00    -     -
    6  "SI"           :        0.00     -     -     -     -     -    1.00    -
    7  "E"            :        0.00     -     -     -     -     -     -    1.00
    8  DIASPORE       :  -1047775.33    2.00  1.00  1.00    -     -     -     -
    9  KALSILITE      :  -2256465.94    4.00  1.00    -    1.00    -    1.00    -
   10  KAOLINITE      :  -4366185.33    9.00  2.00  4.00    -     -    2.00    -
   11  ALEUCITE       :  -3229951.25    6.00  1.00    -    1.00    -    2.00    -
   12  BLEUCITE       :  -3229405.33    6.00  1.00    -    1.00    -    2.00    -
   13  NEPHELINE      :  -2231922.39    4.00  1.00    -     -    1.00  1.00    -
   14  PYROPHYLLITE   :  -5929821.26   12.00  2.00  2.00    -     -    4.00    -
   15  A-QUARTZ       :   -957912.89    2.00    -     -     -     -    1.00    -
   16  B-QUARTZ       :   -957821.08    2.00    -     -     -     -    1.00    -
   17  COESITE        :   -953829.50    2.00    -     -     -     -    1.00    -
   18  CORUNDUM       :  -1745597.28    3.00  2.00    -     -     -     -     -
   19  ALPHA CRISTOBALI :   -955432.80    2.00    -     -     -     -    1.00    -
   20  BETA CRISTOBALIT :   -955771.70    2.00    -     -     -     -    1.00    -
   21  LOW TRIDYMITE  :   -955698.13    2.00    -     -     -     -    1.00    -
   22  HIGH TRIDYMITE :   -955863.33    2.00    -     -     -     -    1.00    -
   23  ANDALUSITE     :  -2704783.72    5.00  2.00    -     -     -    1.00    -
   24  KYANITE        :  -2704158.53    5.00  2.00    -     -     -    1.00    -
   25  SILLIMANITE    :  -2705131.37    5.00  2.00    -     -     -    1.00    -
   26  ALBITE         :  -4167512.31    8.00  1.00    -     -    1.00  3.00    -
   27  K-FELDSPAR     :  -4205701.06    8.00  1.00    -    1.00    -    3.00    -
   28  MUSCOVITE      :  -6320272.46   12.00  3.00  2.00  1.00    -    3.00    -
   29  PARAGONITE     :  -6276324.68   12.00  3.00  2.00    -    1.00  3.00    -
   30  JADEITE        :  -3187647.18    6.00  1.00    -     -    1.00  2.00    -
   31  STEAM          :   -363605.93    1.00    -    2.00    -     -     -     -
   32  OXYGEN         :   -122337.01    2.00    -     -     -     -     -     -
   33  HYDROGEN       :    -57124.59     -     -    2.00    -     -     -     -
```

For each phase found in the database that belongs to the chemical system defined by the bulk composition, This table shows its name, the apparent ΔG and the composition in terms of the components. The number in the first column is the internal phase-number, used to identify the phase.

The first nc lines (nc=number of components) are fictive "phases" made of the components and represent the initial solution to the equilibrium problem. (Ignore "E")

G (apparent ΔG) = $\Delta_a G = \Delta_f H^o + \int_{T_o}^{T} Cp\, dT - T \cdot S^o - T \cdot \int_{T_o}^{T} \frac{Cp}{T}\, dT + \int_{P_o}^{P} V\, dP$

```
----------------
solution phases:
----------------

----------------------
  1  FSP            :              solution model:  from external subroutine + Margules type excess function
                                   info: external+margules

     1  ALBITE         ( 26)   A(Ab)  = X(Ab)*(1-X(An)**2)

     2  K-FELDSPAR     ( 27)   A(Kfs) = X(Or)*(1-X(An)**2)

    Margules parameters:  W(122) =     11392.56       W(112) =     19902.56
                          K= 0.00                     K= 0.00
```

Line 1: FSP: Name of solution, as defined in the database. The number in front is the internal solution- phase-number, used to identify the solution-phase. This is solution-phase Nr. 1.

Part of this solution model is calculated in an external subroutine (located in the file fsol.f). In addition Margules-Parameters are used to describe its non-ideality.

Line 2: The first enemember of the solution is "ALBITE". (The internal phase number of ALBITE is 26).
Line 3: The second enemember of the solution is " K-FELDSPAR ". (The internal phase number of K-FELDSPAR is 27).

The activity model printed at the end of the lines is a text provided as optional information by the external subroutine. This may be a formula, a comment or simply a reference to some publication.

Line 4: The non-ideality of the solution is expressed as a Margules type excess function.

$$\Delta G^{ex} = \sum W^G \cdot \frac{x_{k_1} \cdot x_{k_2} \cdot \ldots \cdot x_{k_p}}{(s)^K}$$

In this case the excess-function at 600 °C and 4000 Bar is: $X_{ab} \cdot X_{KFsp}^2 \cdot (11392.56) + X_{ab}^2 \cdot X_{KFsp} \cdot (19902.56)$

For both terms $S=X_{ab}+X_{Kfsp}=1$, and $K=0$ (defined in the database)

```
---------------------
   2  WHITE MICA     :           solution model:  ideal one site mixing + Margules type excess function
                                 info: ideal+margules
      MUSCOVITE       [Z]:Si,Si,Si,Al
      PARAGONITE      [Z]:Si,Si,Si,Al

      1  MUSCOVITE       ( 28)   A(Ms) = X(Ms)

      2  PARAGONITE      ( 29)   A(Pg) = X(Pg)

   Margules parameters:  W(122) =     16858.00        W(112) =       7958.00
                         K= 0.00                     K= 0.00
```

Line 1: WHITE MICA: Name of solution, as defined in the database. The number in front is the internal solution-phase-number, used to identify the solution-phase. This is solution-phase Nr. 2.

LIne 2 and 3: Because the database contains information on site occupancies, these are printed. (in this case they are not used to define the activities). The configrational part of this solution model is and ideal solution (a=x) In addition Margules-Parameters are used to describe its non-ideality.

Line 4: The first enemember of the solution is " MUSCOVITE ". (Its internal phase number is 28).
Line 5: The second enemember of the solution is " PARAGONITE ". (Its internal phase number is 29).
The configurational part of the activity models printed at the end of the lines are derived from the information given in the database.
When defining solution models it is crucial to check this output and control that the interpretation of the model corresponds to the intension of the user.

Line 6 and 7: The non-ideality of the solution is expressed as a Margules type excess function.

$$\Delta G^{ex} = \sum W^{G} \cdot \frac{x_{k_1} \cdot x_{k_2} \cdot \ldots \cdot x_{k_p}}{(s)^K}$$

In this case the excess-function at 600 ^oC and 4000 Bar is: $X_{pa}^2 \cdot X_{mu} \cdot (16858.00) + X_{pa} \cdot X_{mu}^2 \cdot (7958.00)$
For both terms $S=X_{pa}+X_{mup}=1$, and $K=0$ (defined in the database)

```
----------------------
 equilibrium assemblage:
 ----------------------

  P =  4000.00 bar       P(Gas) =  4000.00 bar     T =  600.00 C    =  873.15 K
  stable phases:    5    loop =    7    loop2 =    1    max.phases =    51    gcalc =      8508    blkshift = 9.23706E-14
  G(-) = 3.41061E-13     G(System) = -232709781.02    stepsize = 0.00000E+00    R =     8.3143000
```

P	Pressure
P(Gas)	Gases may have a different pressure. (see input description)
T	Temperature in C and K

stable phases	Calculated number of stable phases
loop	Number of iterations
loop2	Number of secondary iterations
max.phases	Maximal number of phases simultaneously considered in any loop.
gcalc	Number of calls to subroutine gcalc (Calculation of ΔG of solution phases)
blkshift	Measure of difference in Bulk between beginning and end of calculation
G(-)	The change of the total G in the last iteration.
G(System)	The apparent ΔG of the system.
Stepsize	Last initial stepsize.
R	Gas constant.

```
        phase            N        mol%                             x           x        activity     act.(x)
        -----            -        ----                             -           -        --------     -------
  0  1  FSP_Ab         6.083286   3.897461      ALBITE         0.962060    9.62060E-01  9.67371E-01  9.67371E-01
                                                K-FELDSPAR     0.037940    3.79400E-02  4.41922E-01  4.41922E-01

  0  2  WHITE_MICA_Ms  13.916714  8.916210      MUSCOVITE      0.701976    7.01976E-01  7.40464E-01  7.40464E-01
                                                PARAGONITE     0.298024    2.98024E-01  7.33208E-01  7.33208E-01

                       [Si(Z)]   = 0.750000   [Al(Z)]   = 0.250000


 15  0  A-QUARTZ       93.916714  60.170898
```

Commented run of Theriak

```
25  0  SILLIMANITE          6.083286    3.897461

31  0  STEAM               36.083286   23.117969
```

phase   Stable phases. The two numbers in front are the indices used by the program. For solution phases the
        first number is zero, for non-solution phases the second number is zero.
        To the names of stable solution phases the abbreviation of the dominant endmember is appended.
N   Number of moles of stable phase.
mol%   mol% of stable phase (not very useful)
x   If the stable phase is a solution phase, the concentrations of the endmembers are listed. (in two different
        formats).
Activity Activity calculated from: -R*T*ln(ai) = G(i), where G(i) is the Gibbs free energy of the endmember i
        relative to the stable assemblage.
act.(x)   Activity calculated as a function of composition.

Activity and act.(X) should be identical within the precision of the calculation.
If a solution phase has sites defined, their occupancies will also be listed.

```
----------------------------------------
 volumes and densities of stable phases:
----------------------------------------

 solid phases      N       volume/mol  volume[ccm]   vol% |    wt/mol      wt [g]     wt %  | density [g/ccm]
 ------------
 FSP_Ab          6.0833     101.8995    619.8838   12.3282 |  262.8342   1598.8954  11.6674 |   2.579347
 WHITE_MICA_Ms  13.9167     141.1169   1963.8841   39.0576 |  393.5074   5476.3296  39.9618 |   2.788520
 A-QUARTZ       93.9167      22.7846   2139.8526   42.5572 |   60.0843   5642.9200  41.1774 |   2.637060
 SILLIMANITE     6.0833      50.0649    304.5588    6.0570 |  162.0456    985.7696   7.1933 |   3.236713
                                     ----------  -------- |            ----------  -------- | ----------
 total of solids                       5028.1794  100.0000 |            13703.9146  100.0000 |   2.725423


 gases and fluids    N      volume/mol  volume[ccm]           wt/mol      wt [g]              density [g/ccm]
 ----------------
 STEAM          36.0833      23.6579    853.6533             18.0153     650.0505               0.761492
```

The output of volumes and weights is separated for solids and gases. vol% and wt% are only calculated for the
solids. Solids are defined in the database in the secion "MINERAL DATA" and gases in "GAS DATA". Because
both sections have identical input, one may chose liberally which phase is a "solid" and which is a "gas".

```
---------------------------
 H2O content of stable phases:
---------------------------
                                                        | wt% of    wt% of    wt% of
 solid phases      N      H2O[pfu]   H2O[mol]   H2O [g]  | phase     solids    H2O.solid
 ------------
 WHITE_MICA_Ms  13.9167     1.000    13.9167   250.7135 |  4.57813   1.82950   100.0000
                                   --------  ---------- |           --------
 total H2O in solids                13.9167   250.7135 |            1.82950

                                                        | wt% of
 gases and fluids   N      H2O[pfu]   H2O[mol]   H2O [g]  | phase
 ----------------
 STEAM          36.0833     1.000    36.0833   650.0505 | 100.00000
```

The output of H_2O content is separated for solids and gases. Solids are defined in the database in the secion
"MINERAL DATA" and gases in "GAS DATA". Because both sections have identical input, one may chose
liberally which phase is a "solid" and which is a "gas". (e.g. melts)

```
----------------------------------------
 compositions of stable phases [ mol% ]:
----------------------------------------

                    O          AL         H          K          NA         SI         E
 FSP_Ab          61.538462   7.692308   0.000000   0.291846   7.400462  23.076923   0.000000
 WHITE_MICA_Ms   57.142857  14.285714   9.523810   3.342743   1.419162  14.285714   0.000000
 A-QUARTZ        66.666667   0.000000   0.000000   0.000000   0.000000  33.333333   0.000000
 SILLIMANITE     62.500000  25.000000   0.000000   0.000000   0.000000  12.500000   0.000000
 STEAM           33.333333   0.000000  66.666667   0.000000   0.000000   0.000000   0.000000
 TOTAL:          58.024691   7.407407  12.345679   1.234568   1.234568  19.753086   0.000000


 -------------------------
 elements in stable phases:
 -------------------------

                    O          AL         H          K          NA         SI         E
 FSP_Ab          48.666287   6.083286   0.000000   0.230800   5.852486  18.249858   0.000000
 WHITE_MICA_Ms  167.000569  41.750142  27.833428   9.769200   4.147514  41.750142   0.000000
 A-QUARTZ       187.833428   0.000000   0.000000   0.000000   0.000000  93.916714   0.000000
 SILLIMANITE     30.416429  12.166572   0.000000   0.000000   0.000000   6.083286   0.000000
 STEAM           36.083286   0.000000  72.166572   0.000000   0.000000   0.000000   0.000000
```

```
 total:            470.000000  60.000000 100.000000  10.000000  10.000000 160.000000   0.000000
```

Composition is recalculated that each row has a sum of 100.

```
  activities of all phases:
  -------------------------

         phase               N            G          activity

  S   51  FSP              6.08329E+00  -1.13687E-13  1.00000E+00    9.6206E-01  3.7940E-02
  S   53  WHITE MICA       1.39167E+01  -2.27374E-13  1.00000E+00    7.0198E-01  2.9802E-01
  P   15  A-QUARTZ         9.39167E+01   0.00000E+00  1.00000E+00
  P   25  SILLIMANITE      6.08329E+00   0.00000E+00  1.00000E+00
  P   31  STEAM            3.60833E+01   0.00000E+00  1.00000E+00
  P   -7  "E"              0.00000E+00   0.00000E+00  1.00000E+00
  P   33  HYDROGEN         7.10543E-15   0.00000E+00  1.00000E+00
  -----------------------------------------------------------------
  P   -1  "O"              0.00000E+00   3.06481E+05  4.62701E-19
  P   -2  "AL"             0.00000E+00   4.13887E+05  1.73754E-25
  P   -3  "H"              0.00000E+00   2.85623E+04  1.95574E-02
  P   -4  "K"              0.00000E+00   3.11041E+05  2.46909E-19
  P   -5  "NA"             0.00000E+00   2.67165E+05  1.04078E-16
  P   -6  "SI"             0.00000E+00   3.44950E+05  2.31190E-21
  P    8  DIASPORE         0.00000E+00   7.63688E+03  3.49251E-01
  P    9  KALSILITE        0.00000E+00   3.93377E+04  4.43295E-03
  P   10  KAOLINITE        0.00000E+00   2.40708E+04  3.63084E-02
  P   11  ALEUCITE         0.00000E+00   2.37653E+04  3.78691E-02
  P   12  BLEUCITE         0.00000E+00   2.43112E+04  3.51258E-02
  P   13  NEPHELINE        0.00000E+00   2.00049E+04  6.35681E-02
  P   14  PYROPHYLLITE     0.00000E+00   1.26547E+04  1.74966E-01
  P   16  B-QUARTZ         0.00000E+00   9.18156E+01  9.87432E-01
  P   17  COESITE          0.00000E+00   4.08340E+03  5.69794E-01
  P   18  CORUNDUM         0.00000E+00   1.62119E+03  7.99862E-01
  P   19  ALPHA CRISTOBALI 0.00000E+00   2.48009E+03  7.10612E-01
  P   20  BETA CRISTOBALIT 0.00000E+00   2.14119E+03  7.44572E-01
  P   21  LOW TRIDYMITE    0.00000E+00   2.21476E+03  7.37065E-01
  P   22  HIGH TRIDYMITE   0.00000E+00   2.04956E+03  7.54030E-01
  P   23  ANDALUSITE       0.00000E+00   3.47644E+02  9.53241E-01
  P   24  KYANITE          0.00000E+00   9.72837E+02  8.74584E-01
  P   26  ALBITE           0.00000E+00   2.40823E+02  9.67371E-01
  P   27  K-FELDSPAR       0.00000E+00   5.92837E+03  4.41922E-01
  P   28  MUSCOVITE        0.00000E+00   2.18137E+03  7.40464E-01
  P   29  PARAGONITE       0.00000E+00   2.25285E+03  7.33208E-01
  P   30  JADEITE          0.00000E+00   2.21931E+04  4.70262E-02
  P   32  OXYGEN           0.00000E+00   4.90626E+05  4.45855E-30
  S   62  FSP              0.00000E+00   1.13687E-13  1.00000E+00    9.6206E-01  3.7940E-02
  S   69  WHITE MICA       0.00000E+00  -2.27374E-13  1.00000E+00    7.0198E-01  2.9802E-01
```

The table of activities contains all phases considered in the last loop of the G-minimization.
The first colum is an identifier (P for non-solution phases and S for solution phases)
The second column is the internal phase-number identifying the phase. Note that phases which should not be considered for the minimization have a negative number. (e.g. all fictive "phases" made of the components and used for the initial solution to the equilibrium problem.)

phase names of phases.
N   Number of moles of phase in stable assemblage.
G   Gibbs free energy relative to the stable assemblage.
Activity Activity calculated from: -R*T*ln(a) = G

The remaining columns are the concentration of endmembers for solution phases, in the same order as they are defined in the database.

```
  exit THERIAK
  CPU time:     0h 00m 00.04s
```

Here the program tells you that it took less time to calculate the equilibrium, than you need to read the output.

The Terminal output is also written to the out-file. This is usually called "OUT"