

# OpenCalphad examples version 5

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This is a short description of the macro files used to test and to demonstrate the facilities of this version of OpenCalphad (OC). The macro files and the necessary datafiles are provided with the software.

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# 1 Introduction

OpenCalphad is an initiative of a group of scientists interested to develop a free software for thermodynamic calculations in multicomponent systems. It can be downloaded from

**<http://www.opencalphad.org>**

or the development version from the opencalphad repository at

**<http://www.github.com/sundmanbo/opencalphad>**

There is extensive documentation and several publications[15Sun1, 15Sun2, 16Sun] describing this initiative and the software. For a general description of the Calphad technique and application please read [98Sau] and for a description of thermodynamic modeling and assessments see [07Luk]. For a comprehensive introduction to thermodynamics see [08Hil].

The OC software is modular and includes

- basic libraries for numerics and user interaction,
- the General Thermodynamic Package (GTP) for thermodynamic models,
- the Hillert Minimizer Software (HMS) for equilibrium calculations,
- the Step, Map and Plot (SMP) package for step, map and plotting connected to the GNUPLOT graphical software,
- the assessment facilities (part of several modules) for assessment of experimental and theoretical data in terms of thermodynamic model parameters,
- the Application Software Interface (OCASI) to provide thermodynamic data to other software including multi-threading and an isoC binding for C++ and other programming languages.

The software code is free with a GNU GPL license. Most of the software is written in the new Fortran 08 standard. Any skilled programmer interested to use it in applications, develop or add to the software is welcome. The software has been tested for use in parallel with the OpenMP standard. Anyone interested in using OC in commercial software has to contact the copyright owner for another type of license.

The graphics are generated by GNUPLOT, which is another free software the user must install separately. The OC software creates a command and data file, `ocgnu.plt`, that can be run by GNUPLOT from the OC software. One a few of all facilities provided by GNUPLOT has been implemented in OC but the `ocgnu.plt` file can be edited for users who are interested to explore the extensive facilities of GNUPLOT.

OC has a classical command interface, there is no “click and run” facility. If you prefer that you are welcome to develop one for OC or use a commercial software.

The macro files contain commands to execute the OC software. Study the macros to learn how to calculate various things. They contain comment lines, which start with “@\$” and the macro will pause at lines with a, “@&”. Depending on the OS and the graphics driver installed with GNUPLOT the user may have to click in the graphical window to continue after each plot.

The macros described here are regularly used to test for errors in the software during the development. There is a “super macro” all.OCM which executes all the macros. As shown by the examples there are still many more problems inside OC to fix. Note that some examples perform differently using different compilers and operating system. The development of OC has been on a Windows system using MinGW and GNU Fortran.

## 2 New features

There are very few changes from version 4 in the diagrams except for the isothermal section in example 3.3.6, which can now be plotten in a Gibbs triangle with tie-lines. But the mapping of phase diagrams with tie-lines in the plane has improved significantly.

As OC is now used on many Linux installations which may have different setups for GNU-PLOT there is a new command **enter GNUPLOT-TERMINAL** By default the screen on some Linux systems is the “qt” terminal and on others the “wxt” terminal. The user can change this in the source code or enter his preferred terminal interactively or in a setup macro.

## 3 Macros

Changes in the command structure (new commands, new questions etc) require changes in the macro files and old macro files many not work on a new release and vice versa.

After installing OC please verify your installation by executing all the macros. The database files needed are provided with the macro files.

### 3.1 Single equilibrium calculations

The macros contain single equilibrium calculations. There are no diagrams.

#### 3.1.1 Equilibria in pure Fe

Macro file unary.OCM

Calculation of single equilibrium for a pure element, Fe. The example just shows how to set various conditions of a simple system, including enthalpy,  $H$ . It shows that if you first

makes a calculation for conditions on  $T, P$  and the size of the system  $N$ , you can then set the calculated enthalpy value as condition and release the condition of  $T$  to recalculate the temperature and if you change the value of  $H$  then  $T$  will change and maybe also the stable phase.

### 3.1.2 Testing combination of various conditions for a ternary system

Macro file testcond1.OCM

The ternary system C-Cr-Fe is used to show how different conditions can be combined. The first calculation is made for fix  $T, P$  and mole fractions. Such conditions allow the grid minimizer to be used. For many other sets of condition the grid minimizer cannot be used but for such cases the grid minimizer will automatically be called AFTER the equilibrium has been calculated (when  $T, P$  and mole fractions are known) to check that no grid-point is below the current equilibrium.

We again that one can calculate the same equilibrium by changing one condition for another giving the new condition the value just calculated, and then calculate a new equilibrium changing the value of the new condition.

One condition many thermodynamic software does not allow is to set the mole fraction of a phase, that works with OC. There is a test setting the reference state for the components, setting a phase fix, checking how the driving force for a metastable phase changes with conditions and using enthalpy as condition.

After this it is explained how to calculate the NPLE (Negligible Partition Local Equilibrium) at 1000 K.

Finally some fictitious mobility data are entered and the Darken stability matrix calculated. This matrix consists of all partial derivatives of the chemical potentials with respect to all components,

$$\frac{\partial G_A^\alpha}{\partial N_B} = \frac{1}{N} \left( \frac{\partial^2 G_M^\alpha}{\partial x_A \partial x_B} - \sum_C x_C \left( \frac{\partial^2 G_M^\alpha}{\partial x_C \partial x_B} + \frac{\partial^2 G_M^\alpha}{\partial x_A \partial x_C} \right) + \sum_C \sum_D x_C x_D \frac{\partial^2 G_M^\alpha}{\partial x_C \partial x_D} \right) \quad (1)$$

The formula is derived in the documentation of the minimizer, hms2.pdf. Note that it is symmetric:  $\frac{\partial G_A^\alpha}{\partial x_B} = \frac{\partial G_B^\alpha}{\partial x_A}$ . If at one (or more) of the eigenvalues of the stability matrix is negative the composition of the phase is inside the spinodal, i.e. there is a miscibility gap.

The Darken stability matrix is also necessary to convert mobility data to diffusion coefficients.

### 3.1.3 Equilibria and melting T of a 6 component high speed steel (HSS)

Macro file melting.OCM

Calculations of equilibria in a multicomponent steel using different kinds of conditions. As the previous example it shows the flexible way of setting conditions. First a straightforward calculation with  $T$ ,  $P$  and mole fractions. Then the command **calculate transition** is used to calculate the melting temperature directly.

Then the carbon content of the fcc phase,  $x(\text{fcc}, \text{c})$ , is set as condition rather than the overall carbon content,  $x(\text{c})$ . Then we set the status of the liquid phase as fix with zero amount, and the condition on  $T$  is released to calculate the new melting  $T$ . Then the current value of the enthalpy,  $H$ , is set as condition and the size of the system,  $N$  is released. The equilibrium of the system does not change, just the way we control the system.

In the final calculation the enthalpy of the system is changed and the system response is to change its size, because all other conditions are potentials that is the only way it can change its enthalpy.

### 3.1.4 Saving a calculation on an unformatted file

Macro file save.OCM

A nice facility in OC is the possibility to save a calculation on a file and then read in back and continue the calculations. The file is written as “unformatted” and can only be read by OC. All thermodynamic data, and conditions for all entered equilibria are saved but not yet results from STEP or MAP.

The unformatted file will depend on the version of the OC software, it may not be possible to read a file saved with a different version of OC. It is also fragile because if you have made complicated calculations the data structure may be too involved to be read back again. Keep backups of complicated calculations as macro files.

## 3.2 Property diagram calculations

These are calculations with a single independent axis variable.

### 3.2.1 Diagrams for phase fractions, phase compositions, heat content and heat capacity for a HSS

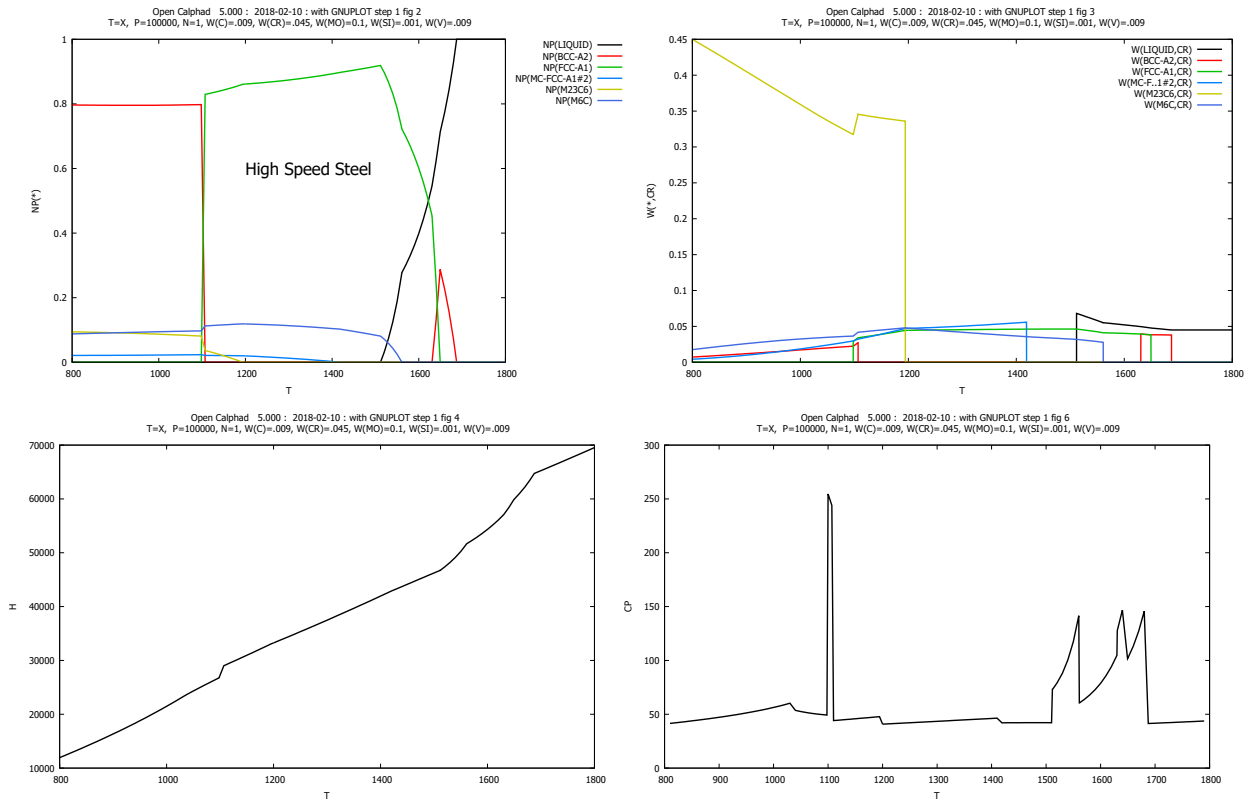
Macro file step1.OCM

A similar steel like in the example 3.1.3 is used. In these steels there is normally a cubic carbide stable and this is described by the same model for FCC phase as the austenite. To make it easier to identify these two phases we can enter a second composition set with additional pre- and suffixes and predefined default composition limits. The software will try to find the composition set with closest default composition if it has two composition sets stable for a phase. We must then also set a default composition for the austenite (the first

composition set).

When we list the result after the equilibrium calculation we find two FCC phases, one with the MC prefix which is high in carbon. That is the cubic carbide, the other FCC phase is the austenite.

Then we set  $T$  as an axis variable with the limits 800 and 1800 K and an increment of 10 K and calculate equilibria along this axis. During the calculation the exact  $T$  value for phase changes is calculated and all calculated equilibria are stored. They can be listed and also the list of all stored node points with phase changes. Any property value or derived symbol for these equilibria can be listed or plotted.



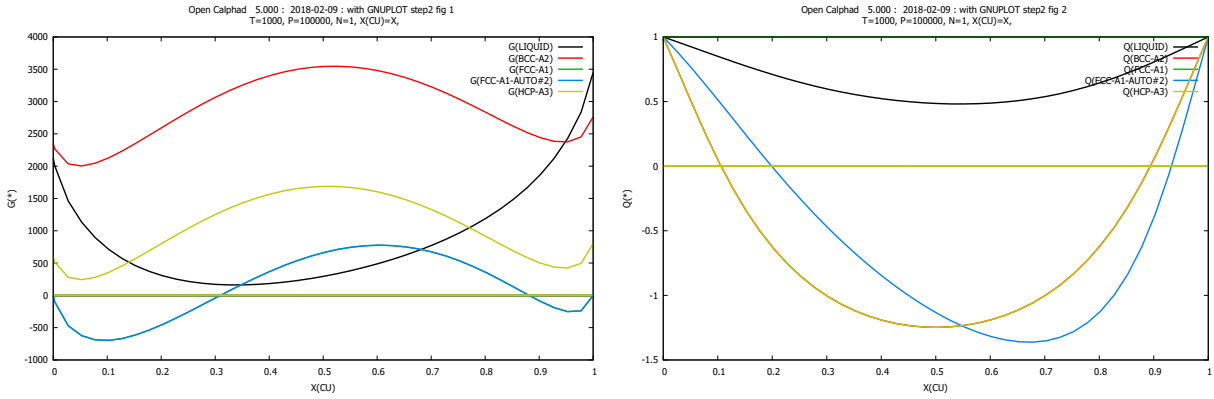
For plotting the GNUPLOT software is used. The OC interface to GNUPLOT uses only a minimum of the extensive facilities of GNUPLOT. The first plot is how the amount (in moles) of the phases varies. The second plot show the Cr content in the stable phases, then a plot of the enthalpy variation and finally we enter and plot a symbol  $C_P = H.T$  which is the partial derivative of the enthalpy with respect to  $T$ , i.e. the heat capacity. Across a phase transition it also includes what is normally called the latent heat, that is the sharp peaks.

### 3.2.2 Diagrams for Gibbs energy curves for Ag-Cu

Macro file step2.OCM



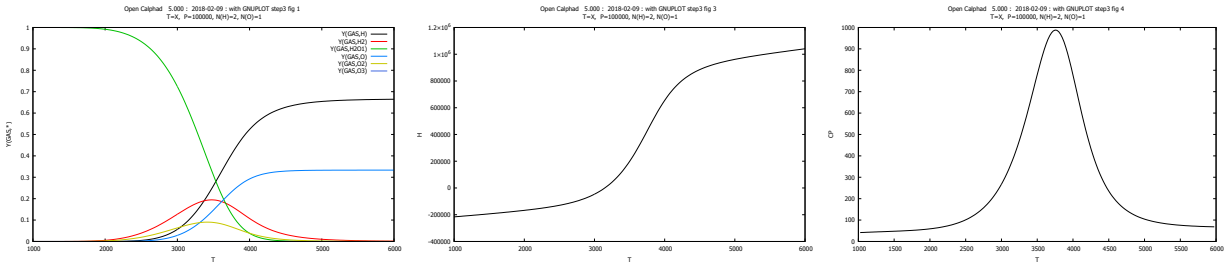
This was my first calculation of Gibbs energy curves with OC so I have kept it. In this and several other plots there are spurious horizontal and vertical lines due to the current simple interface to GNUPLOT. In the right hand diagram the lowest eigenvalue of the Darken stability function, see 3.1.2, called  $Q(\text{phase})$  is plotted. When this is negative the phase is inside the spinodal.



### 3.2.3 Diagrams for gas phase speciation, heat content and heat capacity

Macro file step3.OCM

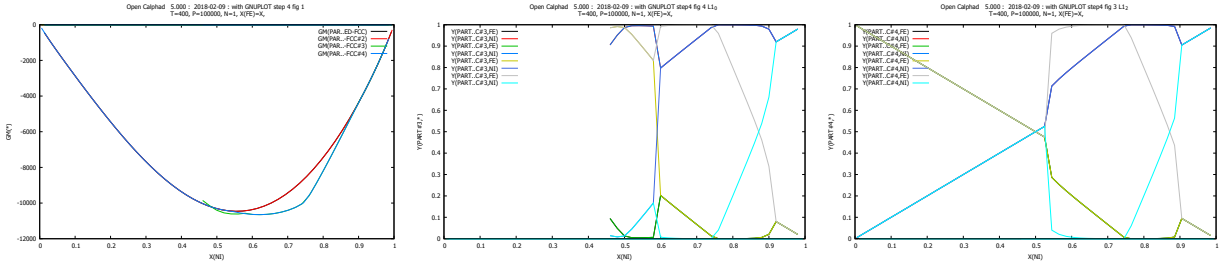
This calculates the speciation of  $\text{H}_2\text{O}$  in a gas phase between 1000 and 6000 K. At low  $T$  the system consists of just the  $\text{H}_2\text{O}$  molecule but around 2000 K it splits up in several molecules and above 5000 K only atomic H and O are present. This changes the configurational entropy and enthalpy and thus also the heat capacity as shown.



### 3.2.4 Diagrams for constitution and Gibbs energy curves for ordered FCC in Fe-Ni using DFT data

Macro file step4.OCM

DFT calculated values for the different ordered forms of FCC in the Fe-Ni system is used to calculate the Gibbs energy curves and sublattice occupancy.

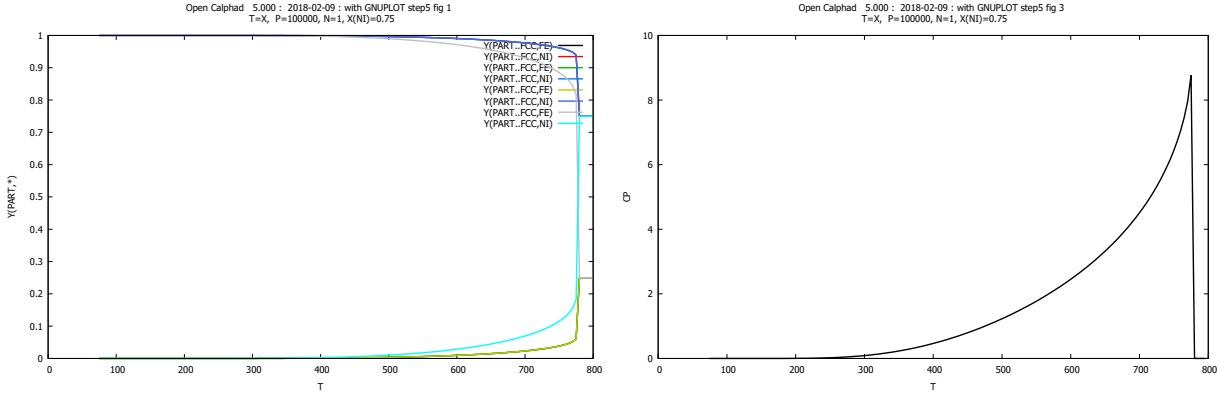


After calculating these diagram the macro uses the command **calculate phase ... const\_adj** to show that this command can calculate the ordering for a single phase giving the overall composition.

### 3.2.5 Diagrams for constitution and heat capacity for DFT calculated ordered FCC in Fe-Ni at Ni<sub>3</sub>Fe

Macro file step5.OCM

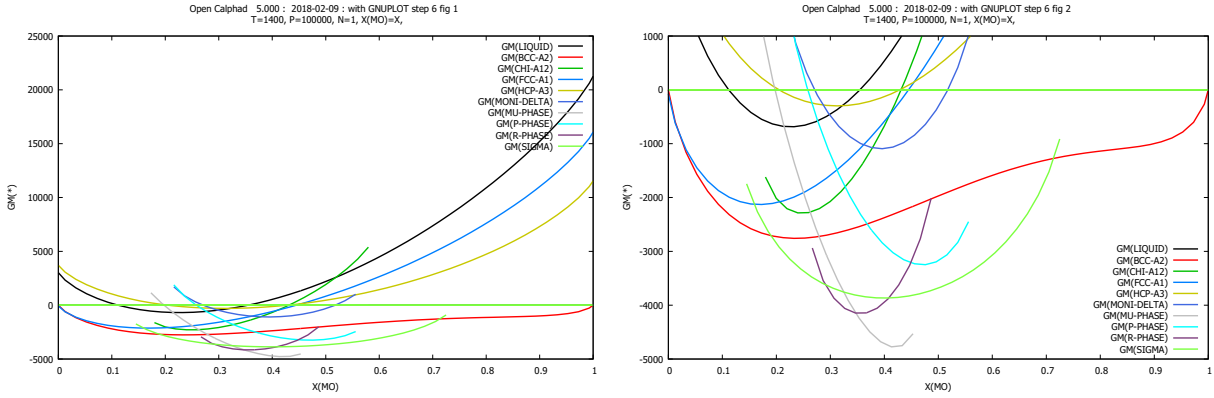
The same DFT data used for a fixed composition FeNi<sub>3</sub> to calculate the constituent fractions for varying  $T$  and their contribution to the heat capacity.



### 3.2.6 Diagram for Gibbs energy curves for Fe-Mo at 1500 K

Macro file step6.OCM

The Gibbs energy curves for the phases in the Fe-Mo system at 1400 K. Note the metastable miscibility gap in the BCC phase.

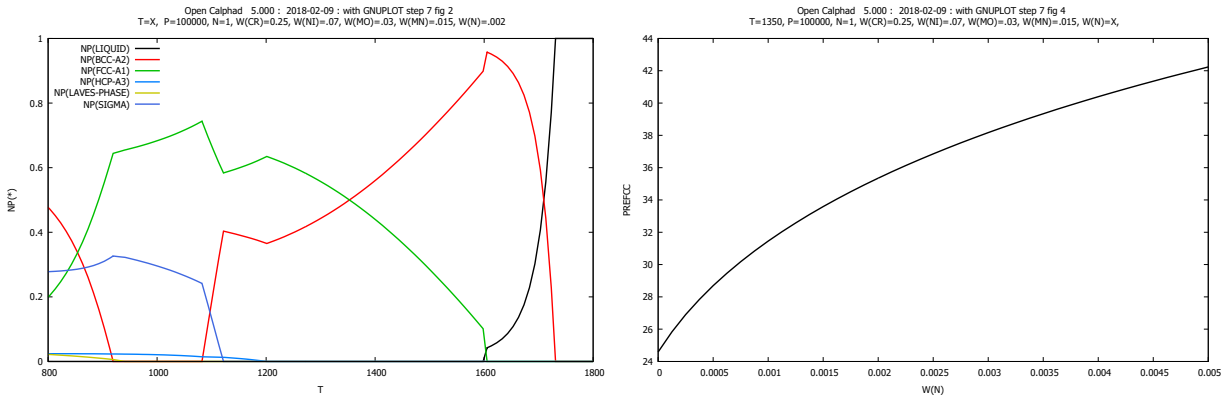


The right hand figure is a magnification.

### 3.2.7 Diagram for phase fractions and PRE for a duplex stainless steel

Macro file step7.OCM

In this example the phase fraction fractions of a duplex stainless steel are calculated and it also show the PRE (Pitting corrosion Resistance Equivalence) varies as a function of the ni-trogen content at temperature of the duplex structure. Rapid cooling from this temperature can preserve the phase amounts and compositions and hence the properties of the alloy.



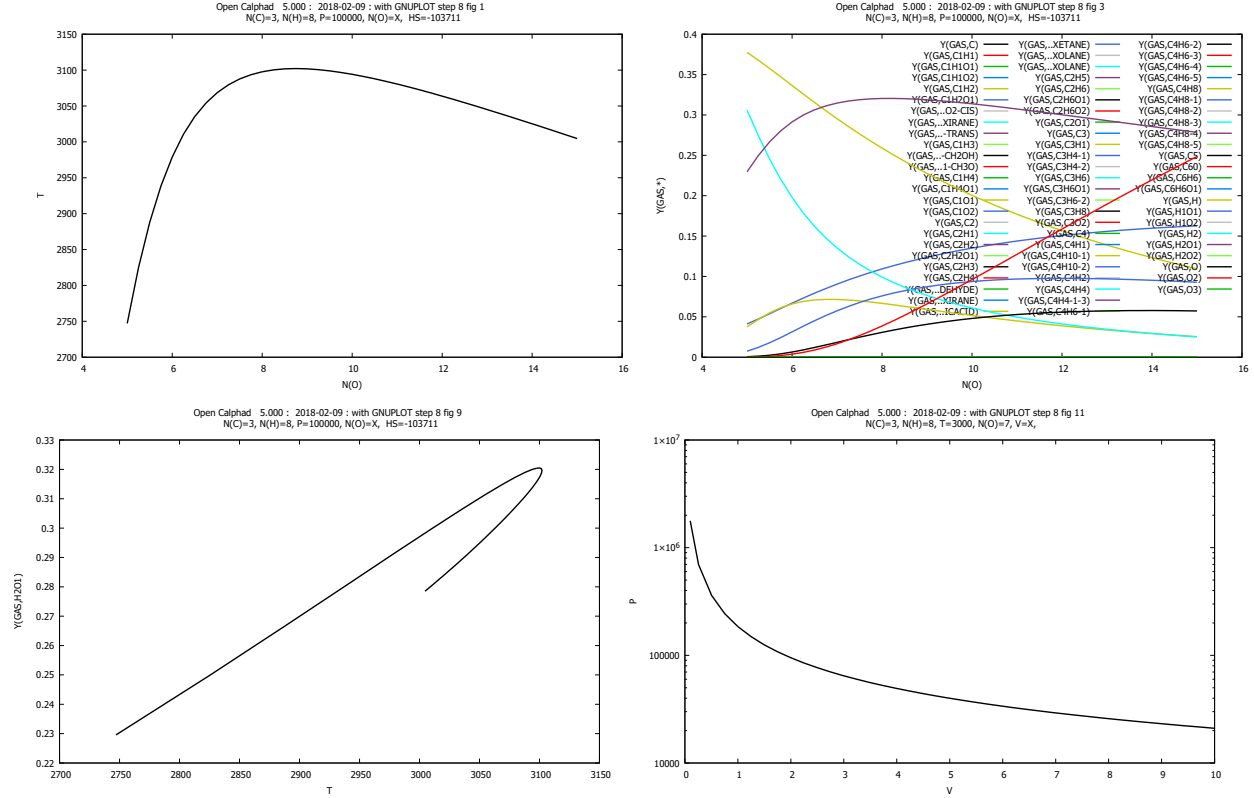
In the right hand figure we have plotted the PRE for FCC defined by the function:  
`ent sym prefcc=100*w(fcc,cr)+300*w(fcc,mo)+1600*w(fcc,n);`

### 3.2.8 Adiabatic flame temperature of propane ( $C_3H_8$ ) as function of the amount of O

Macro file step8.OCM

In this example we first calculate the adiabatic flame temperature of propan ( $C_3H_8$ ) in pure oxygen. First using a stoichiometric fraction of  $N(O)=7$ , then we calculate a diagram for

varying oxygen content. There are about 70 gas species but few of them has any significant amount.



In the lower left diagram above the fraction of  $H_2O$  species in the gas is plotted as function of  $T$ . We also show we can vary the chemical potential of oxygen instead of the amount.

After these diagrams we fix the oxygen amount set a condition on the volume,  $V$ , and allow  $P$  to vary and calculates a P-V diagram for the system. We show that Boyle's law is not valid for this gas because there are reactions between the constituents. That is the lower right diagram above with a logarithmic scaling of the Y axis.

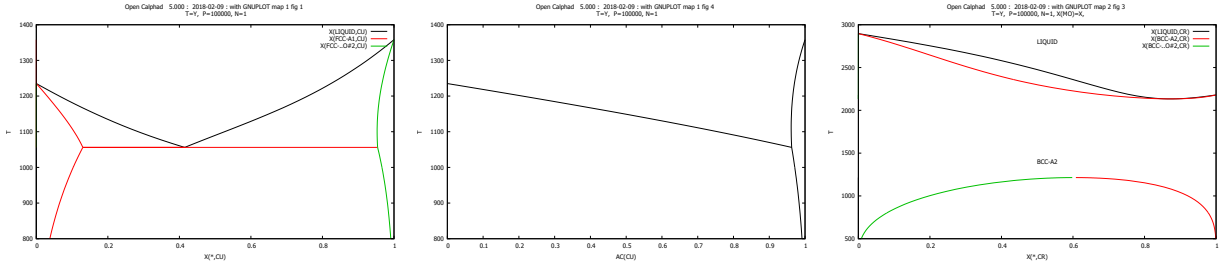
### 3.3 Phase diagram calculations

These now work quite well but are sensitive to the start point. In multicomponent diagrams some lines may be missing.

#### 3.3.1 Phase diagram for Ag-Cu plotted with various axis variables

Macro file map1.OCM

The simple eutectic binary phase diagram for Ag-Cu. There is a miscibility gap in the FCC phase which is detected by the grid minimizer.



One can plot the diagram with different ranges and axis variables, the right hand side use the chemical potential of Cu instead of the amount. The two-phase regions then becomes a line and the invariant eutectic a point where the lines meet. The rightmost diagram is for the Cr-Mo system showing a miscibility gap.

### 3.3.2 Phase diagram for Cr-Mo with miscibility gap

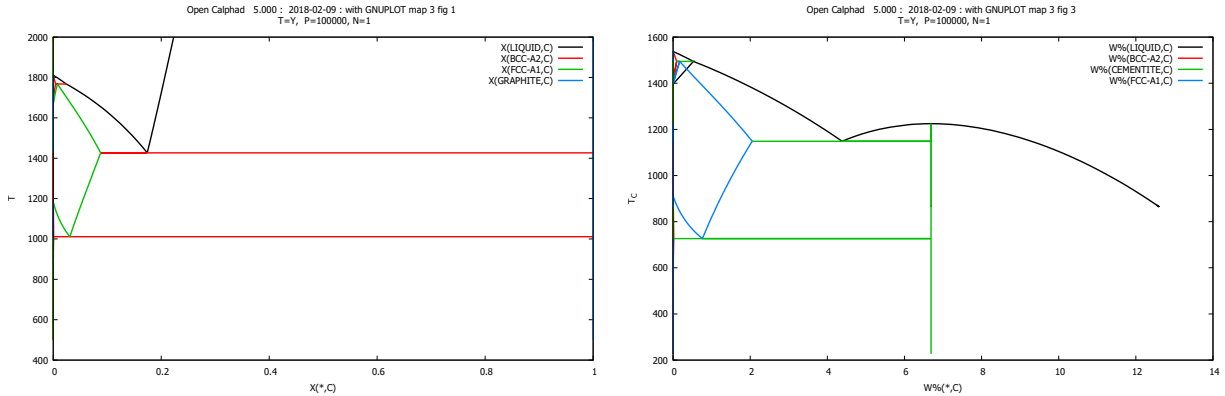
Macro file map2.OCM

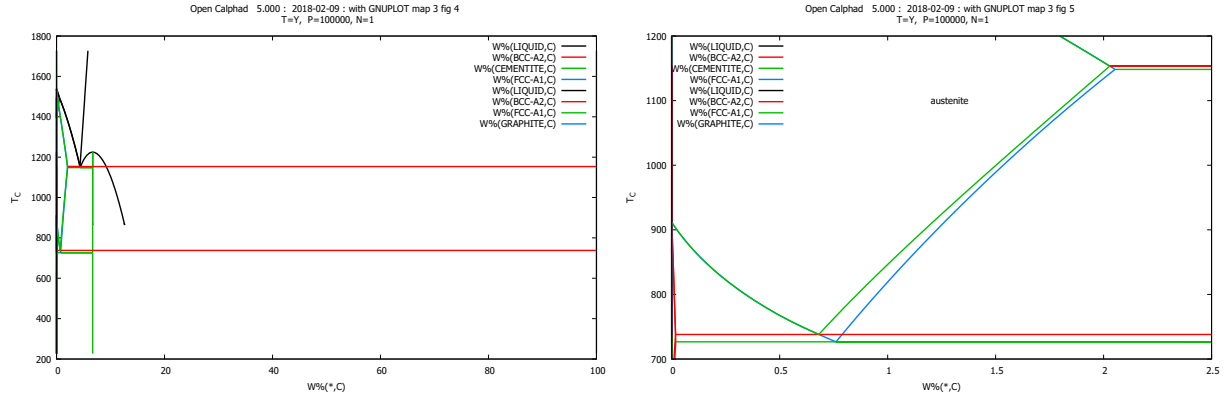
There is a miscibility gap in the BCC phase also in the Cr-Mo system. The phase diagram is shown above. Two start points are needed to calculate this diagram. Note we can add phase labels in the regions by calculating the equilibrium for selected points.

### 3.3.3 Phase diagram for C-Fe

Macro file map3.OCM

The phase diagram for C-Fe system is a must. In the first diagram the whole carbon range up to graphite is included, the second shows the metastable C-Fe system with cementite.



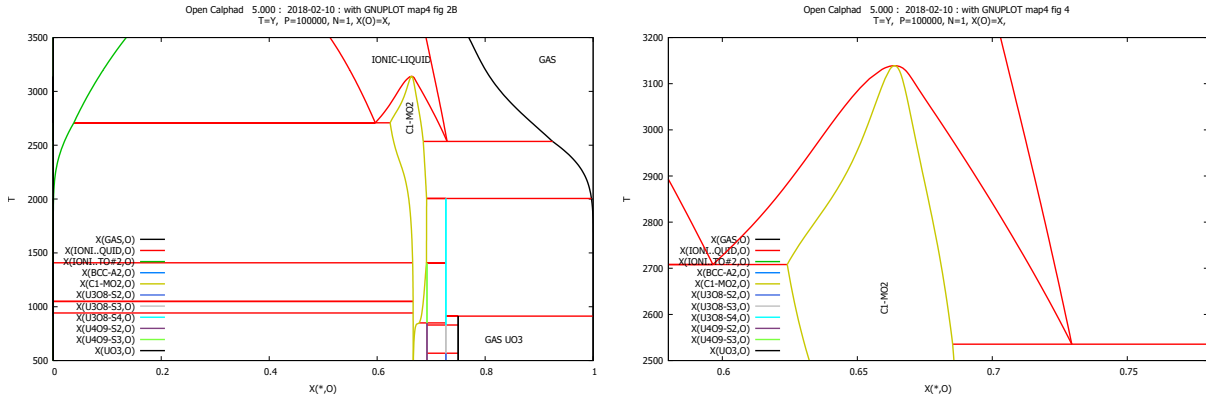


In the third diagram the two diagrams are overlayed for the whole range of carbon and in the last diagram there is just the austenite region with the stable diagram with solubility lines for graphite overlaid with the metastable solubility lines for cementite. Note that the metastable diagram has higher solubility of carbon in the austenite because the carbon activity is greater than unity. The invariant temperatures with bcc and liquid have changed accordingly.

### 3.3.4 Phase diagram for O-U

Macro file map4.OCM

The phase diagram for O-U can now be calculated without problems although the step control is not very good. The macro shows also how to calculate the congruent melting point exactly.

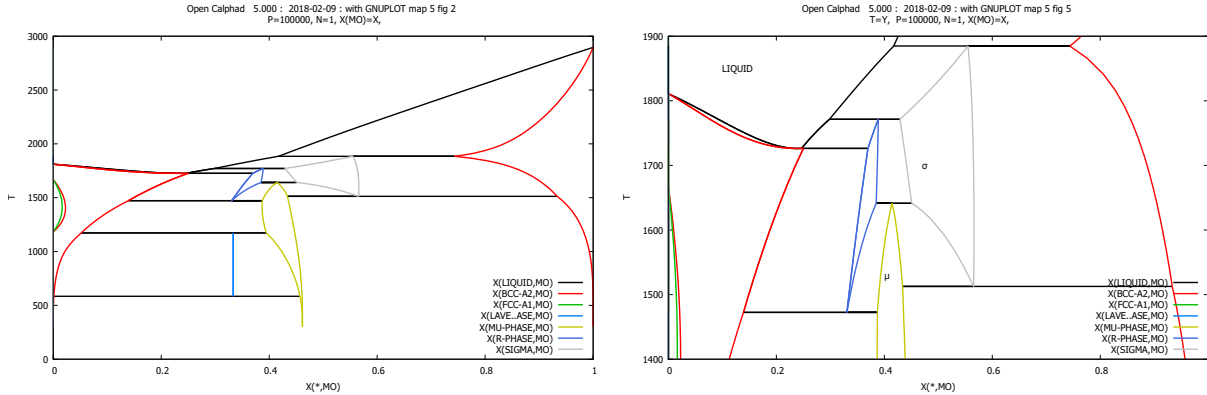


### 3.3.5 Phase diagram for Fe-Mo

Macro file map5.OCM

The Fe-Mo system requires also a separate start point for the  $\gamma$ -loop. The main problem to map it was the peritectic equilibrium between BCC+LIQUID+R-phase, the difference

between the peritectic temperature and the minimum in the bcc/liquid solubility lines is less than 0.2 K.

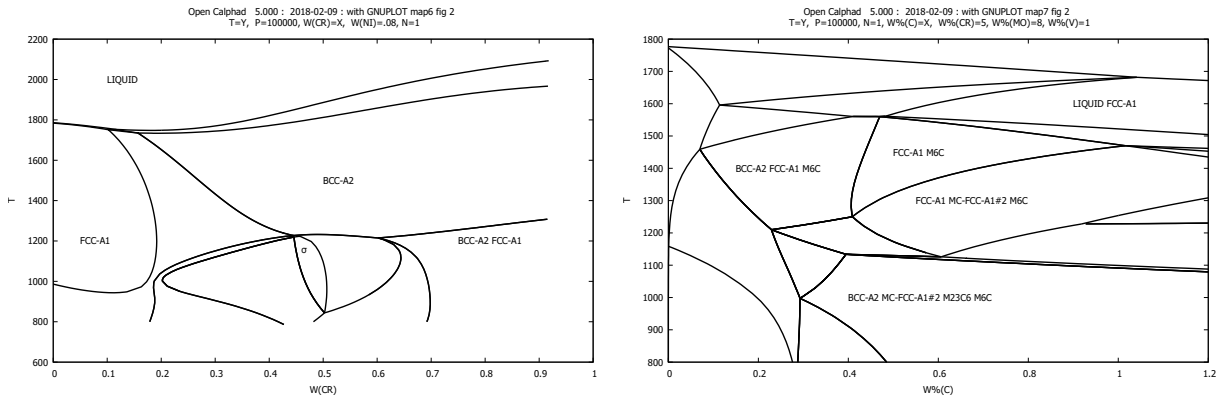


The magnification in the right hand diagram shows that with some GNUMPLOT drivers one can use greek letters.

### 3.3.6 Isopleth phase diagram for an 18-8 stainless steel: Cr-Fe-Ni

Macro file map6.OCM

This is an isopleth for 8 mass% Ni and varying amount of Cr. The calculated section is now correct and phase labels has been added by calculating points inside the diagram.



### 3.3.7 Isopleth calculation of a HSS

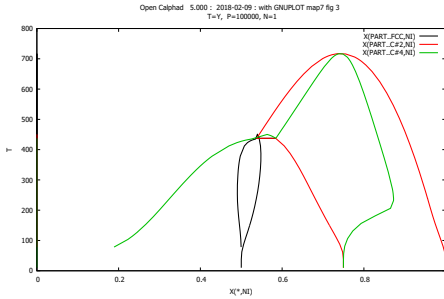
Macro file map7.OCM

The phase diagram for this 6 component High Speed Steel (HSS) on the right above is now almost correct and the phase labels show the stable phases in various regions. The check at the node points if the equilibrium is global has removed all metastable lines. But some lines are still missing and a better step control is needed and probably also generating several start points automatically. So there are things to develop for the next version!

### 3.3.8 Metastable phase diagram for ordered FCC in Fe-Ni using DFT data

Macro file map8.OCM

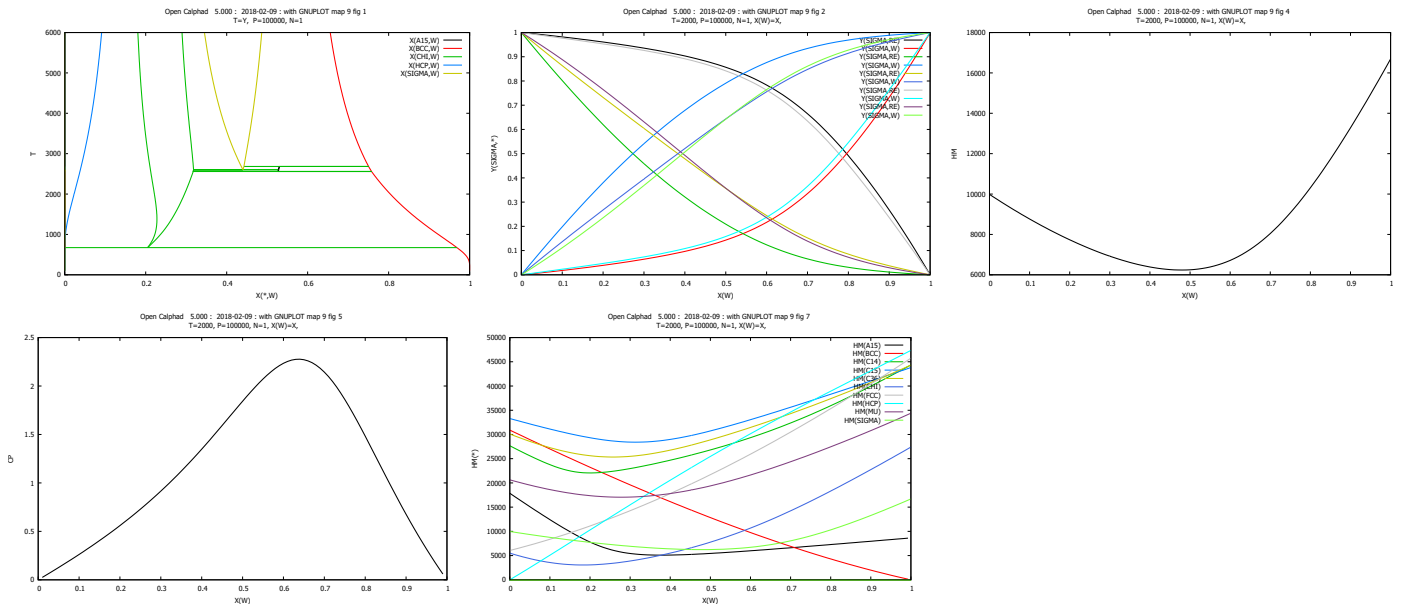
The phase diagram for metastable fcc-Ni using the same DFT data as in the earlier STEP calculations. The  $L_{12}$  and the  $L_{10}$  ordered forms are calculated but there are some metastable extrapolations at the invariant  $A1/L_{12}/L_{10}$ . The miscibility gap on the Al-rich side is sometimes calculated, sometimes it fails. The Fe-rich side is metastable because Fe should be bcc at these temperatures.



### 3.3.9 Metastable Re-W phase diagram based on DFT calculated data

Macro file map9.OCM

DFT calculated data for the TCP phases as well as bcc and hcp in the Re-W system is entered and the phase diagram calculated. Additionally STEP calculations giving site fractions for the  $\sigma$  phase and also the enthalpy and heat capacity. Finally the Gibbs energy and enthalpy curves for all phases are calculated and plotted.



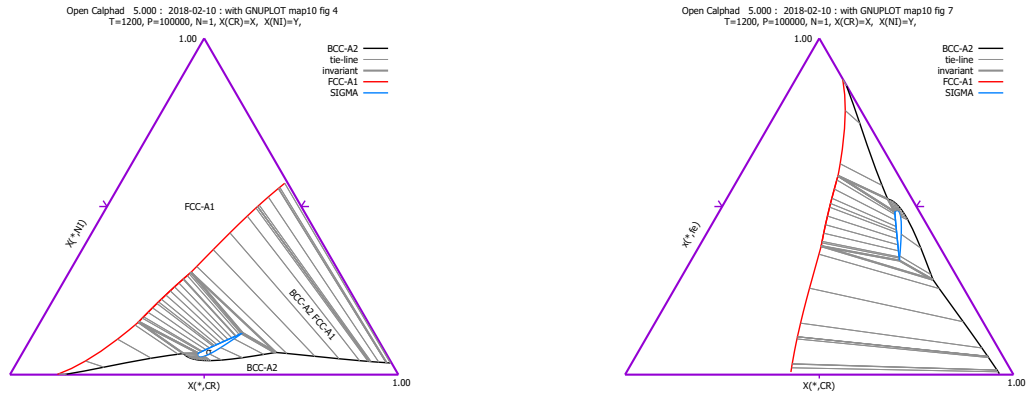


### 3.3.10 An isothermal section in Cr-Fe-Ni

Macro file map10.OCM

The isothermal section of the Cr-Fe-Ni system at 1200 K is calculated and plotted. The unique feature of an isothermal section is that both axis are extensive state variables. In almost all other kinds of diagram one axis is a potential and this have a single value when plotted. That is true also for multicomponent isopleths.

The facility to plot tie-lines is available only for isothermal sections. Note one can write in angles and shift axis variables

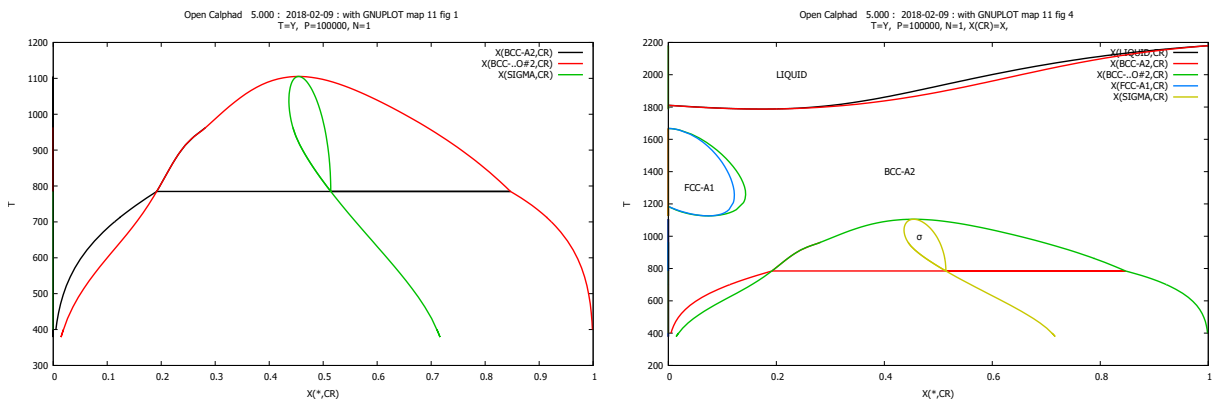


### 3.3.11 The binary Cr-Fe phase diagram

Macro file map11.OCM

The Cr-Fe phase diagram may look simple but is problematic due to the three separate regions and the low  $T$  miscibility gap that closes inside the bcc- $\sigma$  region. Frequently metastable extrapolations of the bcc- $\sigma$  phase boundaries are calculated because the miscibility gap is not detected when calculating from higher  $T$ .

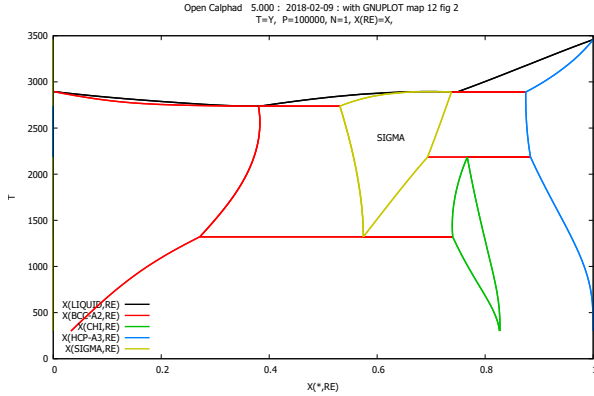
There is no automatic scanning for startpoints in OC so three start points are needed to calculate this diagram.



### 3.3.12 The binary Mo-Re phase diagram

Macro file map12.OCM

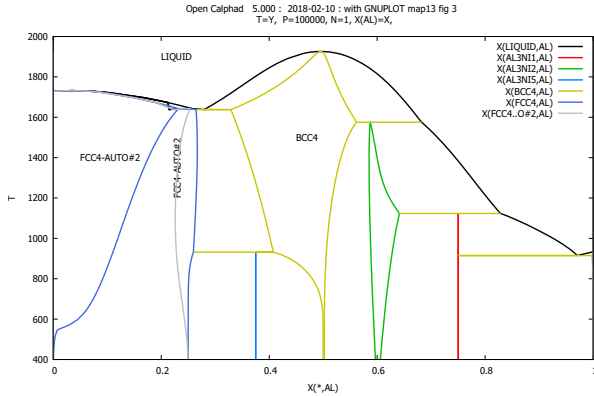
This is just a test reading a database in the PDB format.



### 3.3.13 The binary Al-Ni phase diagram

Macro file map13.OCM

This diagram is a test using the 4 sublattice model including permutations of the model parameters to describe the ordering in FCC and BCC.



## 3.4 Miscellaneous calculations, assessments, parallel etc

This section contains various examples.

### 3.4.1 Calculating 21 equilibria in parallel

Macro file parallel1.OCM

This macro was the first attempt to calculate in parallel using the `enter many_equilibria` command. It is more or less superseded by the next more complex case.

### **3.4.2 Enter a table with 400 equilibria and calculate them in parallel**

Macro file `parallel2.OCM`

In this macro some 400 equilibria are entered using the `enter many_equilibria` command. They are then calculated in parallel (by the parallel version of OC linked with OpenMP). On a PC with 4 kernels and 8 threads the gain in speed is more than a factor of 3 and there are no significant memory leaks.

### **3.4.3 A calculation with 20 elements and 191 phases**

Macro file `allcost.OCM`

This macro calculates a few equilibria with the largest free database I have access to, from the light alloy assessment project COST507. The quality of the database is questionable for multicomponent calculations but many binary and ternary systems are well assessed. The interest was to test OC calculations with a very large system, 20 elements and 191 phases.

### **3.4.4 Setup of an assessment with fictitious binary experimental data**

Macro file `opttest1.OCM`

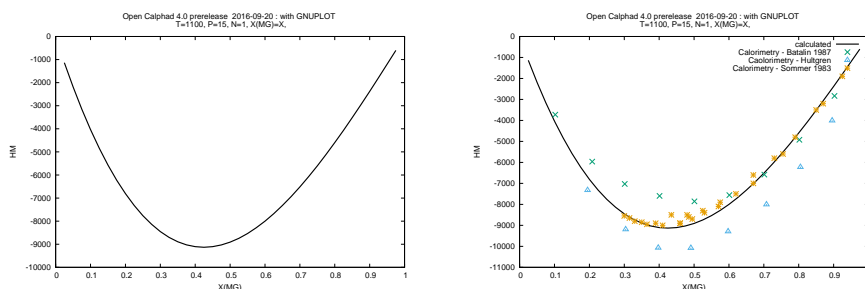
A tentative start of an assessment of a phase in a binary system. It shows how to enter experimental data and optimizing coefficients and how the weighting can change the results.

### **3.4.5 Start of an assessment of the Cu-Mg binary system**

Macro file `opttest2.OCM`

This enters a full set of experimental data for the Cu-Mg system and performs the first step in the assessment by fitting the data for the liquid phase. The `enter many_equilibria` command is used to enter several tables of experimental data.

The experimental data has been converted to an OC macro file from a Thermo-Calc POP file created by Malin Selleby and Christine Guéneau. In OC the experimental data is entered as a macro file. In the figures below the enthalpy of mixing in the liquid has been fitted and plotted together with experimental data.



The SAVE facility, see example 3.1.4, implemented in OC4 is an important facility to save assessments for a current set of model parameters. But save files are fragile, in a later version of OC the data structures may have changed and then it may not be possible to read an old save file.

## 4 Summary

Have fun and help make OC better!

## References

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