OpenCalphad 4
macro examples

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This is a short description of the macro files used to test OpenCalphad (OC) version 4 and to demonstrate its facilities. The macro files and the necessary datafiles are provided with the software.

Contents

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 last release 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 numeric and command handling,

- the General Thermodynamic Package (GTP) for thermodynamic models,

- the Hillert Minimizing System (HMS) for equilibrium calculations,

- the Step, Map and Plot (SMP) package for step, map and plotting connected to the GNUPLOT graphical software,

- the assessment routines (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 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. For the use of OC in commercial software another license is needed.

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. I have not bothered to implement all facilities provided by GNUPLOT 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 please use a commercial software or you are welcome to develop one for OC.

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 the 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 used using MinGW on a Windows system.

2 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. The commands here are for OC version 4.

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

2.1 Single equilibrium calculations

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

2.1.1 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.

Currently there is a bug that one cannot combine a condition on the mass of the system (B) and the enthalpy. Another bug is that OC cannot step across a phase boundary in a unary (or binary) system. It can step across a change in the set of stable phases for multicomponent systems as shown in several examples.

2.1.2 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 show 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 shown 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,

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

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.

2.1.3 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(fcc,c), is set as condition rather than the overall carbon content, x(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.

When the enthalpy of the system is changed the size of the system changes as that is the only way it can change its enthalpy.

2.1.4 Saving a calculation on an unformatted file

Macro file save.OCM

A new 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 "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 file will depend on the version of the OC software, it may not be possible to read a file saved in 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.

2.2 Property diagram calculations

These are calculations with a single independent axis variable.

2.2.1 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 2.1.3 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 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.
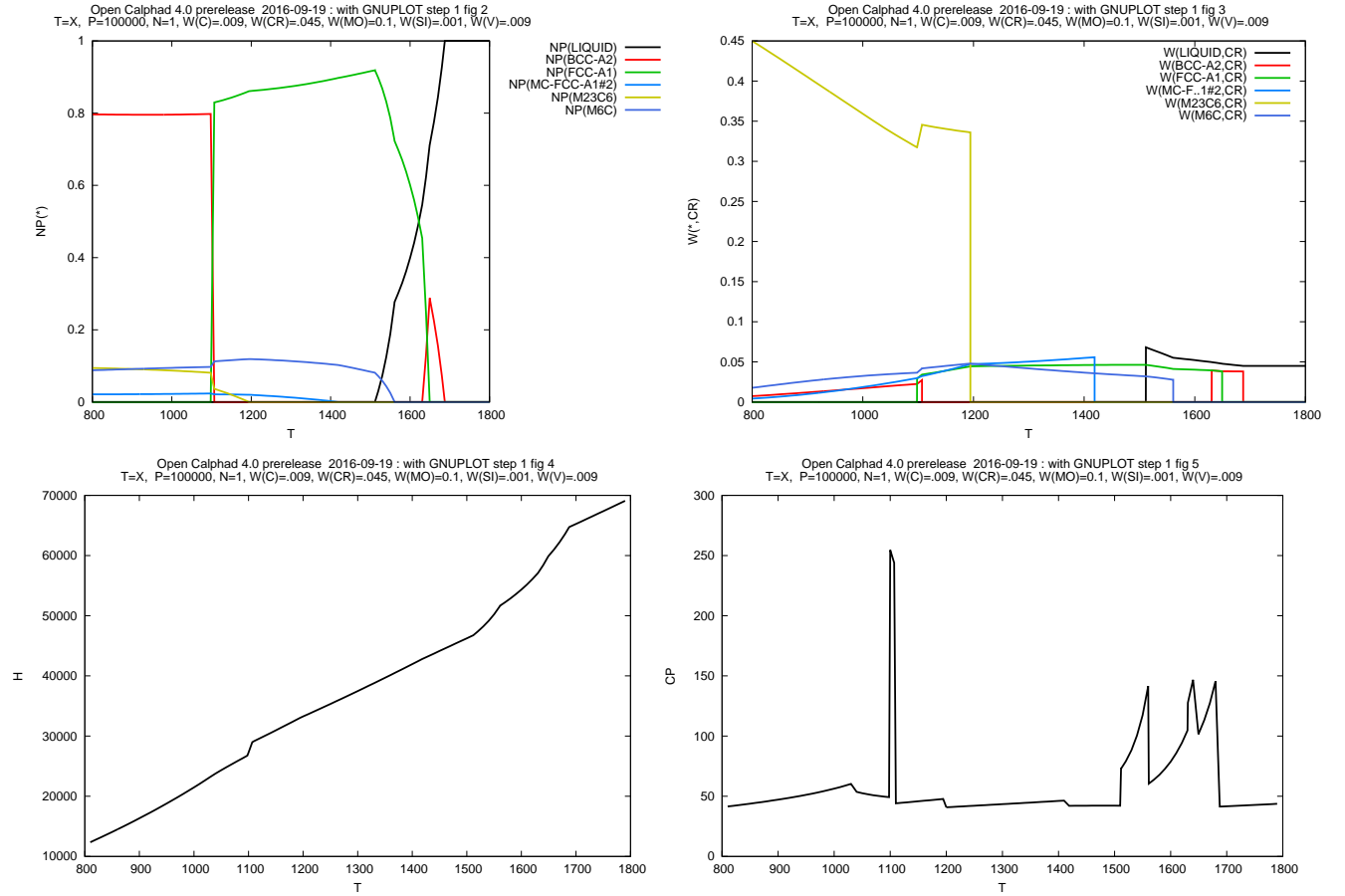
For plotting the GNUPLOT software is used. The OC interface to GNUPLOT uses only a minimum of the extensive facilities of GNUPLOT. The first plot is how the amount (in moles) of the phases varies. The second plot show the Cr content in the stable phases, then a plot of the enthalpy variation and finally 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.

2.2.2 Diagrams for Gibbs energy curves for Ag-Cu
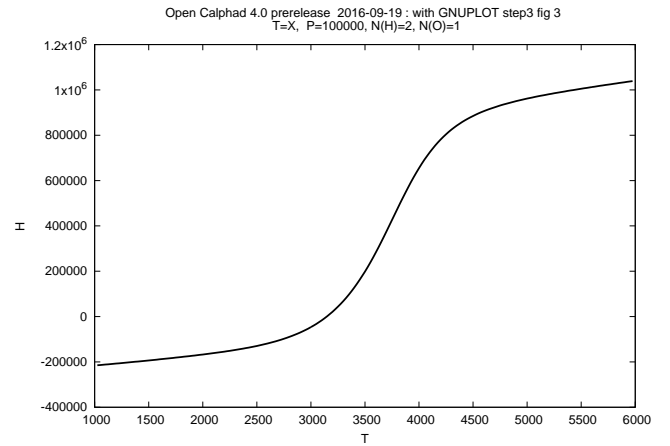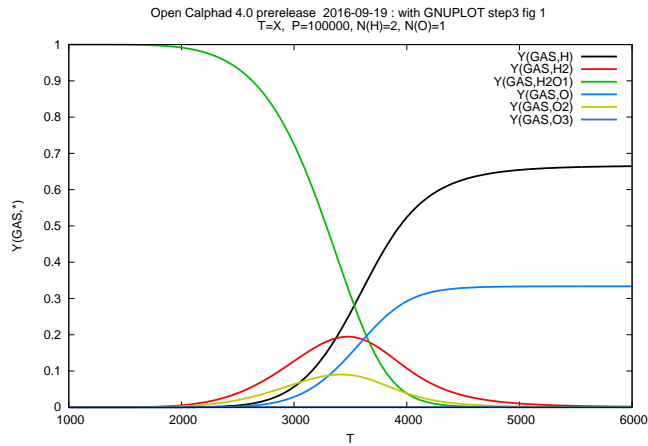
Macro file step2.OCM

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 2.1.2, called Q(phase) is plotted. When this is negative the phase is inside the spinodal.
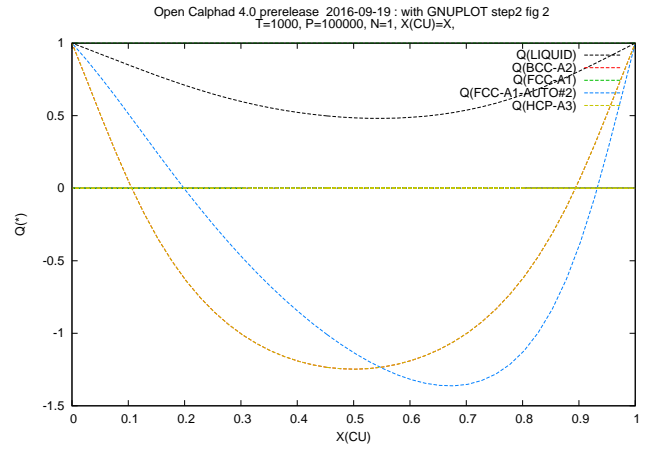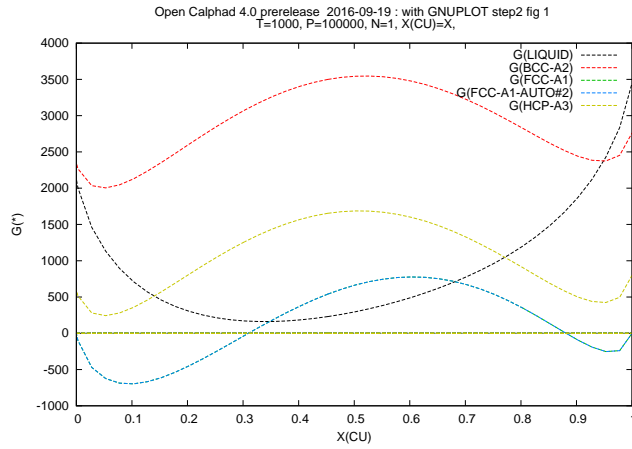
2.2.3 Diagrams for gas phase speciation, heat content and heat capacity

Macro file step3.OCM

This calculates the speciation of H_2O in a gas phase between 1000 and 6000 K. At low T the system consists of just the H_2O 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.
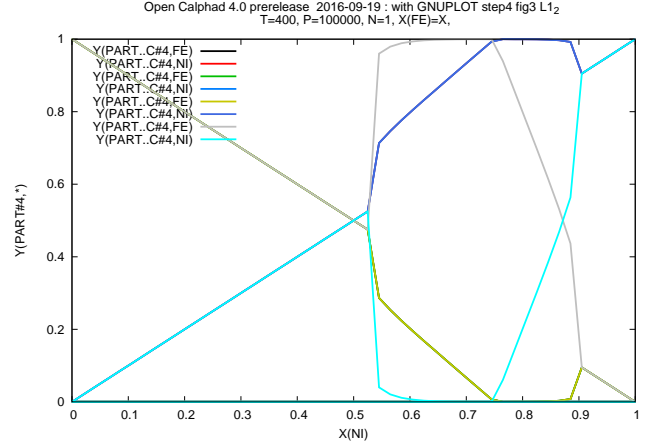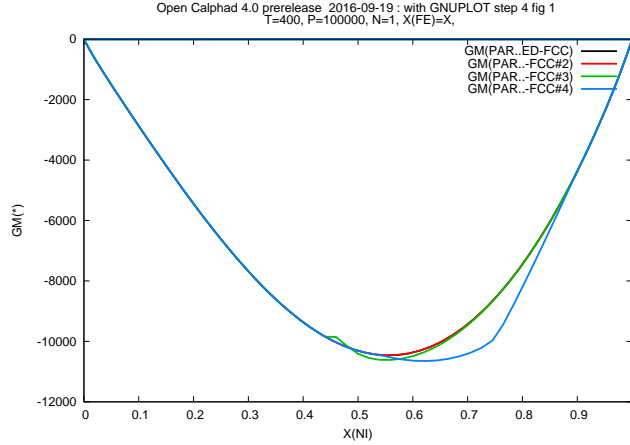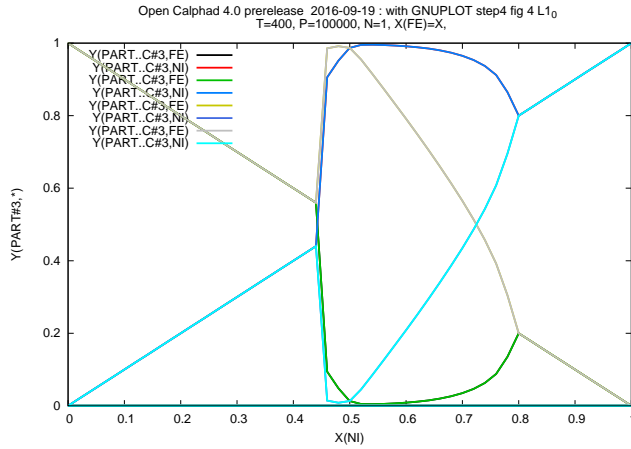

9
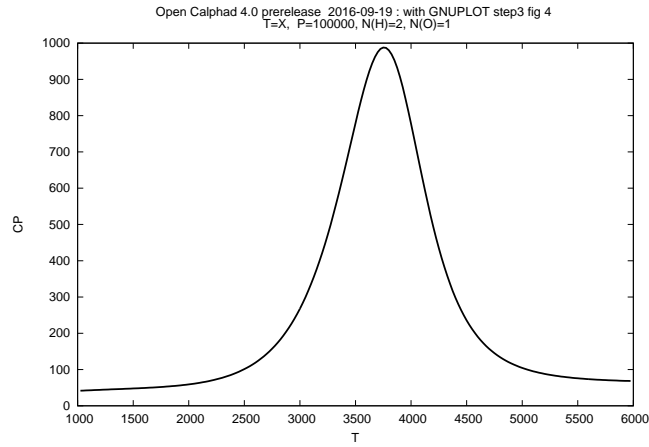
2.2.4 Diagrams for constitution and Gibbs energy curves for ordered FCC in Fe-Ni using DFT data

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.

Open Calphad 4.0 prerelease 2016-09-19 : with GNUPLOT step4 fig 4 L1$_0$
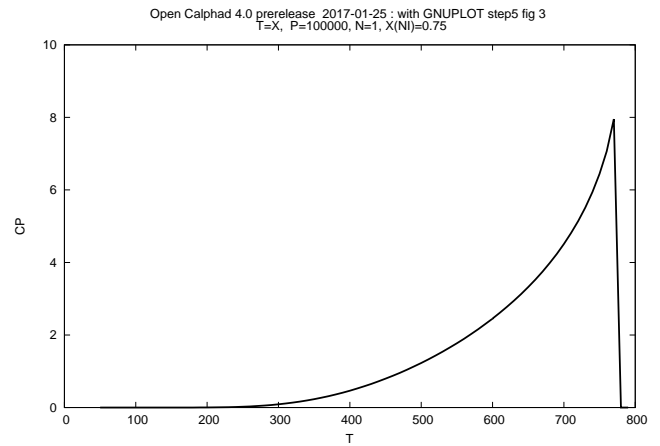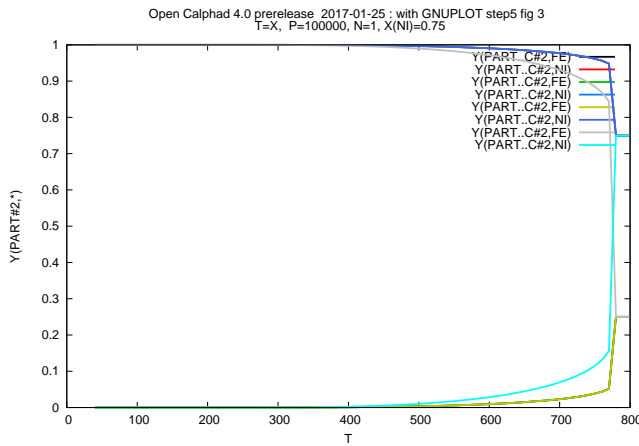T=400, P=100000, N=1, X(FE)=X,

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.

2.2.5 Diagrams for constitution and heat capacity for DFT calculated ordered FCC in Fe-Ni at Ni$_3$Fe

Macro file step5.OCM

The same DFT data used for a fixed composition FeNi$_3$ to calculate the constituent fractions for varying T and their contribution to the heat capacity.

Open Calphad 4.0 prerelease 2017-01-25 : with GNUPLOT step5 fig 3
T=X, P=100000, N=1, X(NI)=0.75

Open Calphad 4.0 prerelease 2017-01-25 : with GNUPLOT step5 fig 3
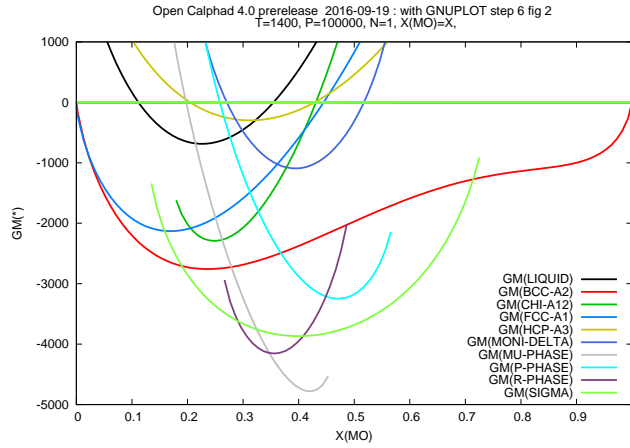T=X, P=100000, N=1, X(NI)=0.75

2.2.6 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.

2.2.7 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 nitrogen 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.
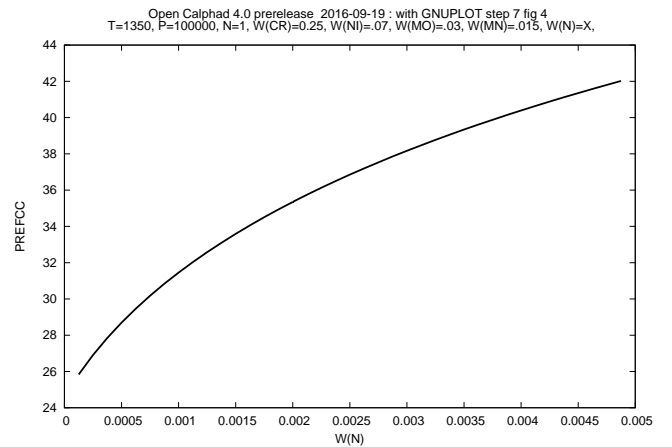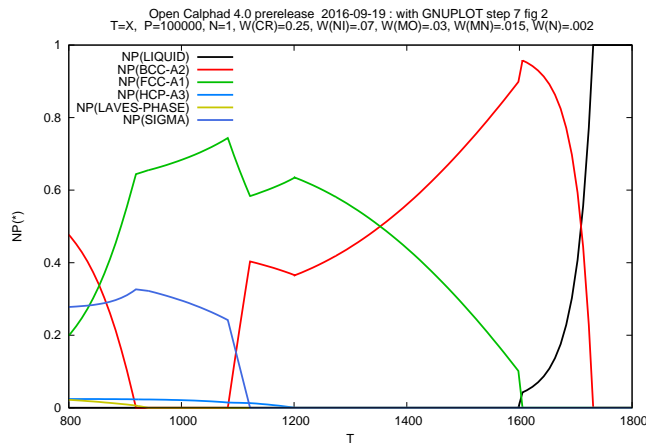

2.2.8 Adiabatic flame temperature of propane (C_3H_8) as function of the amount of O

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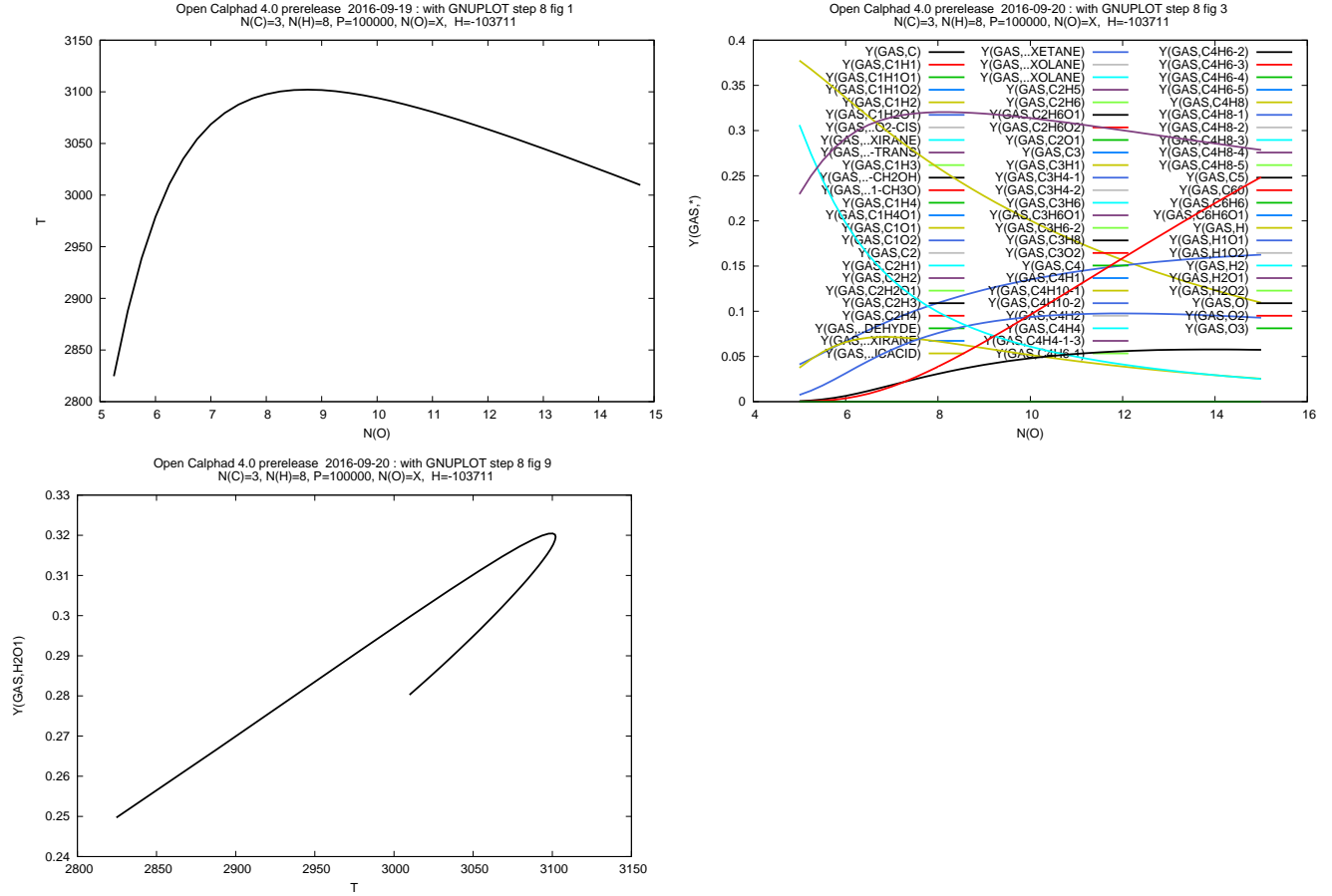
In the last diagram above the fraction of H_2O species in the gas is plotted as function of T. We also show we can vary the chemical potential of oxygen instead of the amount.

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 fr this gas because there are reactions between the constituents.
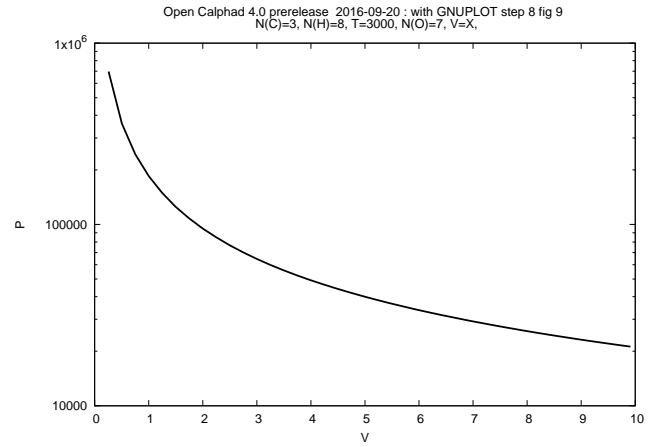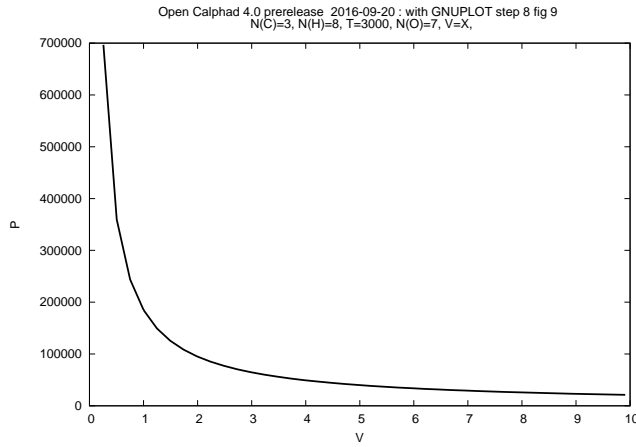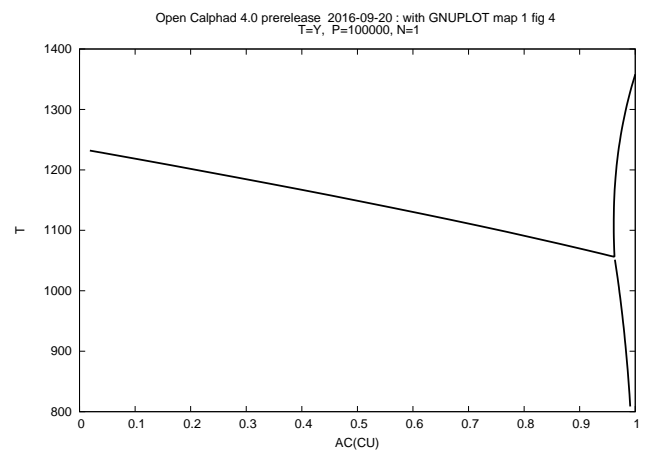
2.3 Phase diagram calculations

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

2.3.1 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 region then becomes a line.
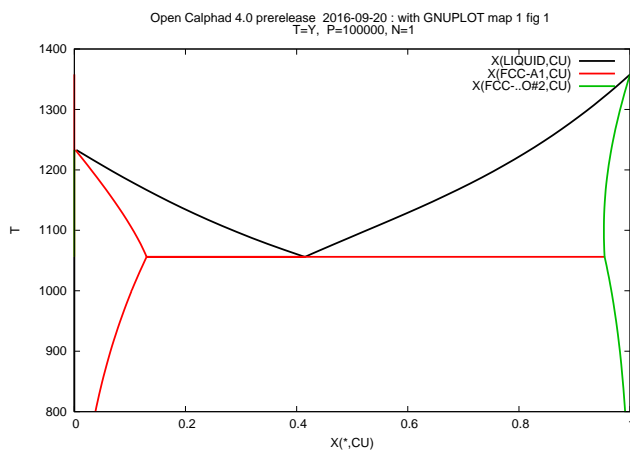
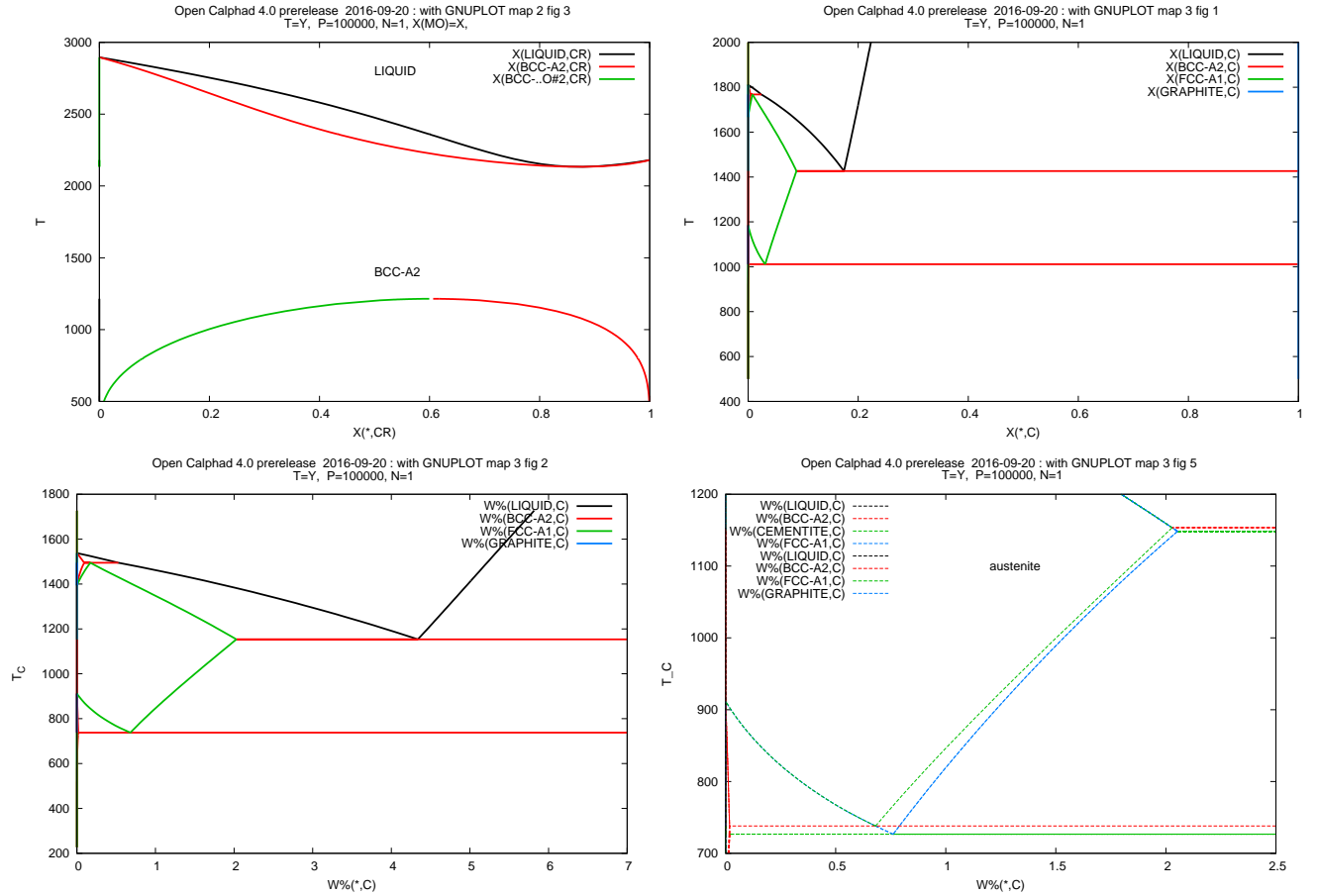### 2.3.2 Phase diagram for Cr-Mo with miscibility gap

Macro file map2.OCM

There is a miscibility gap in the BCC phase also in the Cr-Mo system. As can be seen the mapping fails to calculate the top of this miscibility gap. Note we can add phase labels in the regions by calculating the equilibrium for selected points.
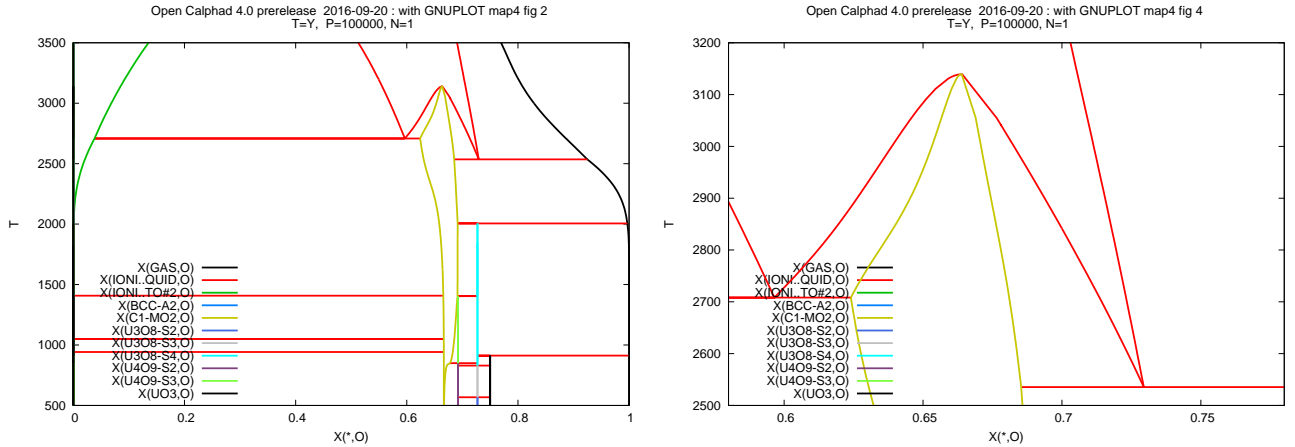

2.3.3 Phase diagram for C-Fe

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 a zoom up to 7 mass% C is shown. In the third diagram the austenite region is shown with the stable diagram with graphite overlaid with the metastable diagram with cementite instead of graphite.

2.3.4 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 note very good. The macro shows also how to calculate exactly the congruent melting point.

2.3.5 Phase diagram for Fe-Mo

Macro file map5.OCM

The Fe-Mo system requires also a separate start point for the γ-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 second diagram shows that with some GNUPLOT drivers one can use greek letters.
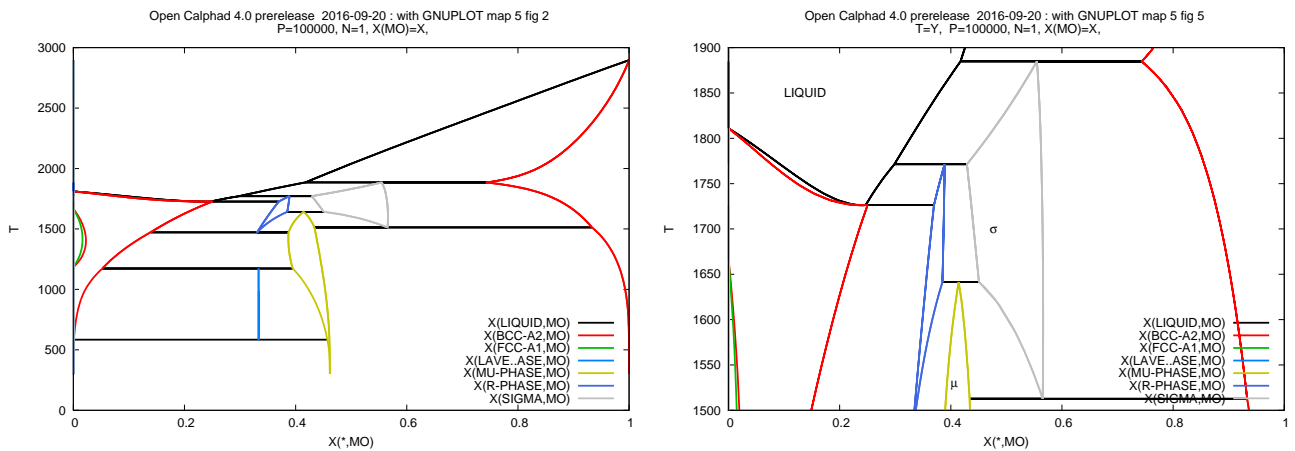
2.3.6 Isopleth phase diagram for an 18-8 stainless steel: Cr-Fe-Ni

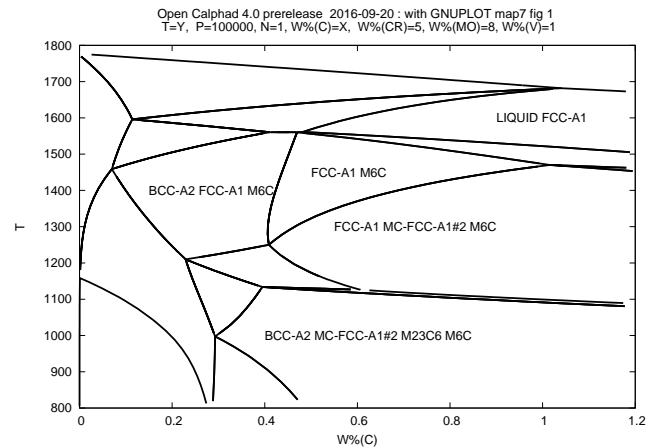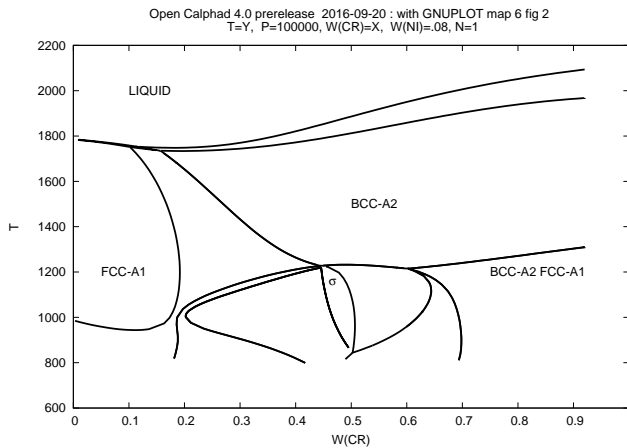Macro file map6.OCM

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.


2.3.7 Incomplete isopleth calculation of a HSS

Macro file map7.OCM

The phase diagram for this 6 component High Speed Steel (HSS) is now almost correct and the phase labels sow 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!

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

Macro file map8.OCM

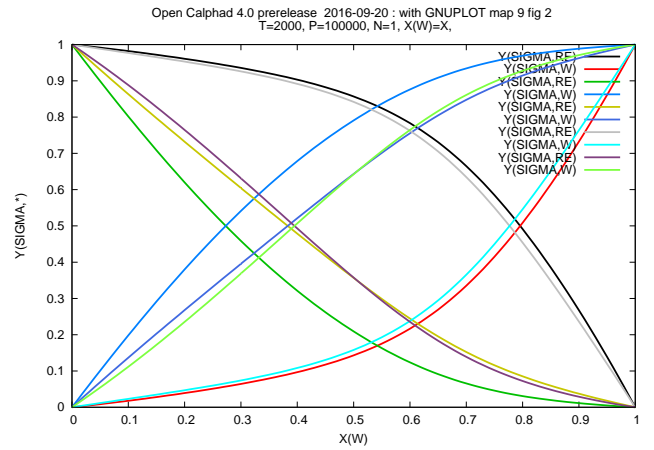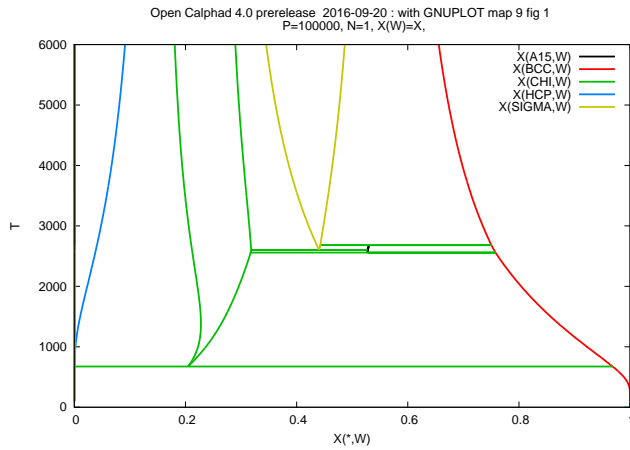The phase diagram for metastable fcc-Ni using the same DFT data as in the earlier STEP calculations. The $L1_2$ and the $L1_0$ ordered forms are calculated but there are some metastable extrapolations at the invariant $A1/L1_2/L1_0$. The miscibility gap on the Al-rich side is sometimes calculated, sometimes it fails. The Fe-rich side is metastable because Fe should be bcc at these temperatures.

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map8 fig 1
T=Y, P=100000, N=1
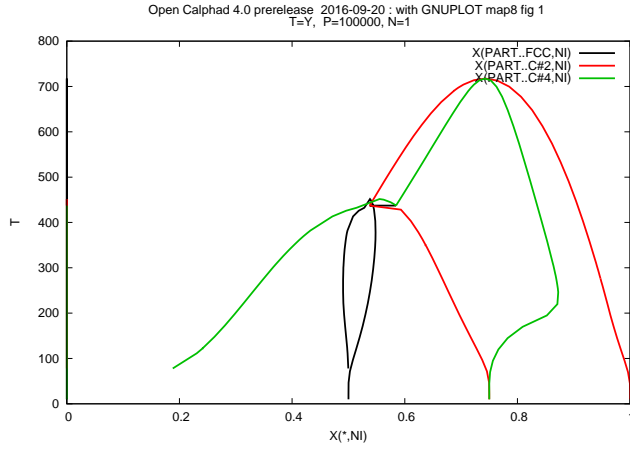
2.3.9   Metastable Re-W phase diagram based on DFT calculated data

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 σ phase and also the enthalpy and heat capacity. Finally the Gibbs energy
and enthalpy curves for all phases are calculated and plotted.

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 9 fig 1
P=100000, N=1, X(W)=X,

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 9 fig 2
T=2000, P=100000, N=1, X(W)=X,

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 9 fig 4
T=2000, P=100000, N=1, X(W)=X,

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 9 fig 5
T=2000, P=100000, N=1, X(W)=X,

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 9 fig 7
T=2000, P=100000, N=1, X(W)=X,

HM(A15)
HM(BCC)
HM(C14)
HM(C15)
HM(C36)
HM(CBB)
HM(FCC)
HM(HCP)
HM(MU)
HM(SIGMA)

2.3.10   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 facitity to plot tie-lines is available only for this type of diagram and there is no triangular diagram available yet.

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Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 10 fig 1
T=1200, P=100000, N=1, X(NI)=Y,

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 10 fig 3
T=1200, P=100000, N=1, X(CR)=X, X(NI)=Y,
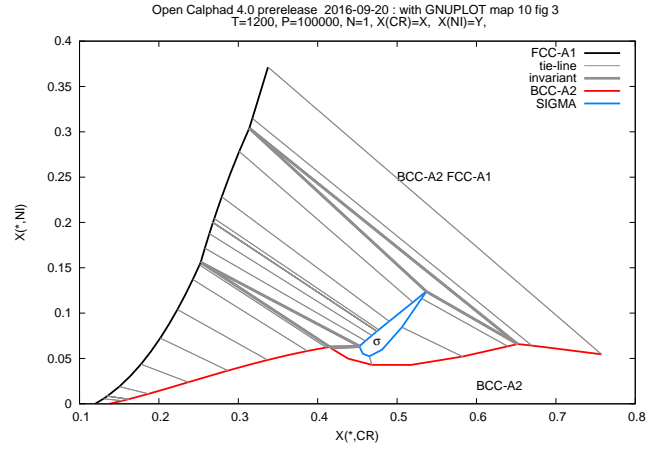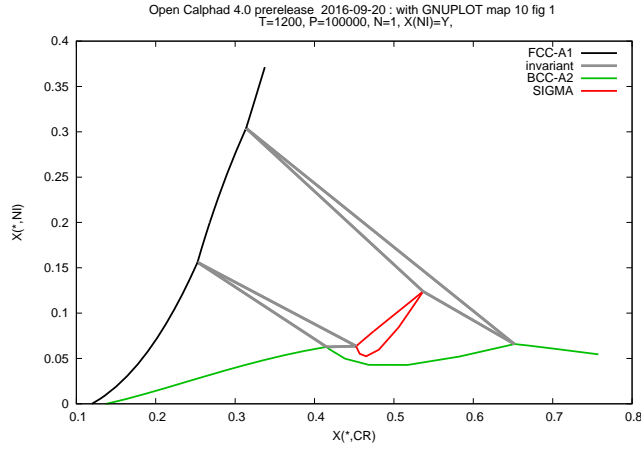
2.3.11   The binary Cr-Fe phase diagram

Macro file map11.OCM

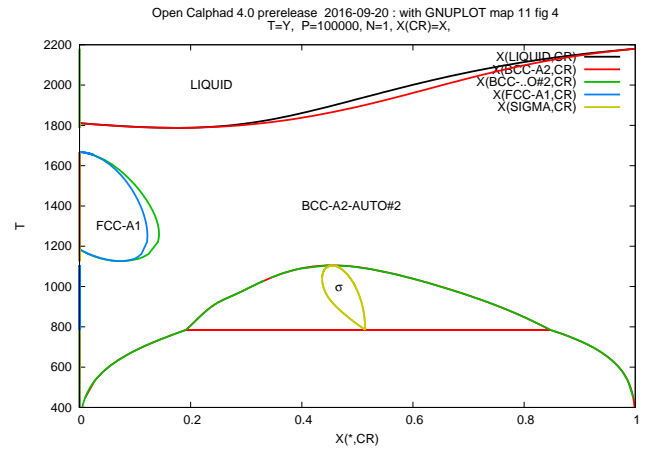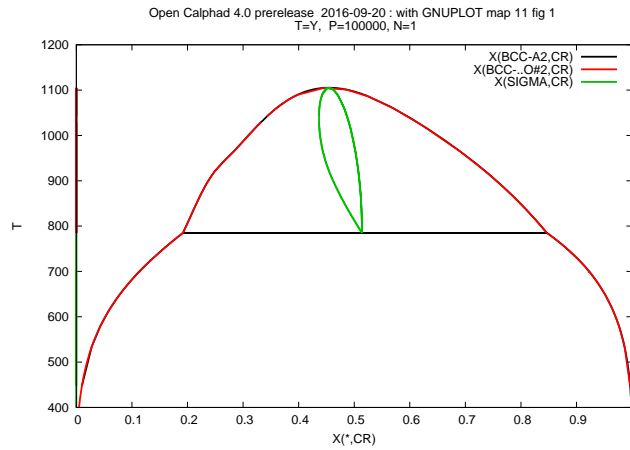The Cr-Fe phase diagram may look simple but is problematic due to the three separate regions and the low T miscibility gap that closes inside the bcc-σ region. Frequently metastable extrapolations of the bcc-σ phase boundaries are calculated because the miscibility gap is not detected when calculating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

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

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 11 fig 1
T=Y, P=100000, N=1

Open Calphad 4.0 prerelease 2016-09-20 : with GNUPLOT map 11 fig 4
T=Y, P=100000, N=1, X(CR)=X,

2.4   Miscellaneous calculations, assessments, parallel etc

This section may contain various examples.

2.4.1 Calculating 21 equilibria in parallel

Macro file parallel1.OCM

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

2.4.2 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 then a factor of 3 and there are no memory leaks.

2.4.3 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.

2.4.4 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.

2.4.5 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. The enthalpy of mixing in the liquid is fitted and plotted together with experimental data.
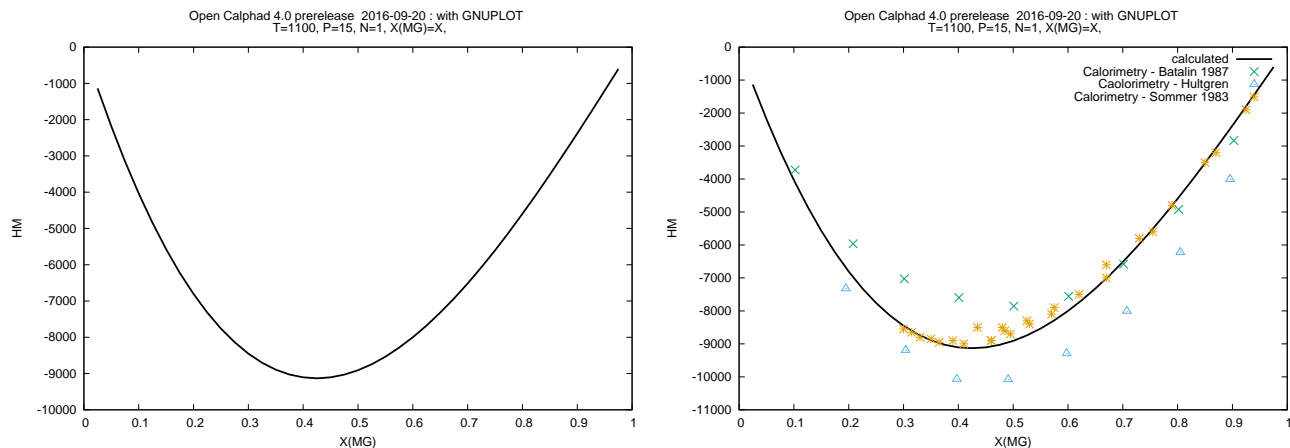
The new SAVE facility, see example 2.1.4, is an important facility to save assessments for a current set of model parameters but it must be tested thoroughly before it can be trusted.

3   Summary

That is all

References

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