

# OpenCalphad examples version 6

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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. A setupfile for Windows can be downloaded from

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

For Linux, MacOS or to use the OC Applications Software Interface (OCASI) the source code can be downloaded from the opencalphad repository at

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

There is extensive documentation and some publications[15Sun1, 15Sun2, 16Sun] describing OC. 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. The macros are useful 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 but regular tests on a Linux systems are made.

## 2 GNUPLOT graphics

OC uses the free GNUPLOT software to plot on the screen and other devices. You must install GNUPLOT before you can obtain any figures.

You can download GNUPLOT from <http://gnuplot.info/download.html>

In OC you can list or enter a GNUPLOT terminal by the command:

—>OC6: **enter gnuplot\_term**

GNUPLOT terminals are: 5

	Name	> command	GNUPLOT options
1	SCREEN	> set terminal wxt	size 840,700 font "Arial,16"
2	PS	> set terminal postscript	color solid fontscale 1.2
3	PDF	> set terminal pdf	color solid size 6,5 enhanced font "Arial,16"
4	GIF	> set terminal gif	enhanced fontscale 0.7
5	PNG	> set terminal png	enhanced fontscale 0.7

Change (exact match required) or enter a new GNUPLOT terminal

Terminal id (8 chars):

The terminals listed above are the default on Windows. On a Linux system they may be different. Before changing anything you should first start GNUPLOT and use the command “**set term**” to list the available terminals on your installation of GNUPLOT.

In OC after giving a PLOT command and specified your axis you can select to plot on any of the the terminal devices listed above (or which you defined yourself) by:

*Options?* /*RENDER*/: **graphics\_format n**

where the number “n” is the gnuplot terminal you wish to use. If you plot on SCREEN you do not need to give this command and in the GNUPLOT window you can select to save the plot on a file in different formats.

## 3 New features

There are a few changes from version 5 in the diagrams except for the isoplethal section that is now plotted with different colors depending on the phase that has zero amount along the line. Mapping is still fragile and often require several start points.

## 4 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 some of the macros. The database files needed are provided with the macro files.

### 4.1 Single equilibrium calculations

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

#### 4.1.1 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.

#### 4.1.2 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 T-zero point where two phases have the same Gibbs energy at the same  $T$  and composition. Such a point is the limit of a diffusionless transformation. There is also an example how to calculate 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.

### 4.1.3 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,  $x(\text{fcc}, c)$ , 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.

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.

#### 4.1.4 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.

## 4.2 Property diagram calculations

These are calculations with a single independent axis variable.

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

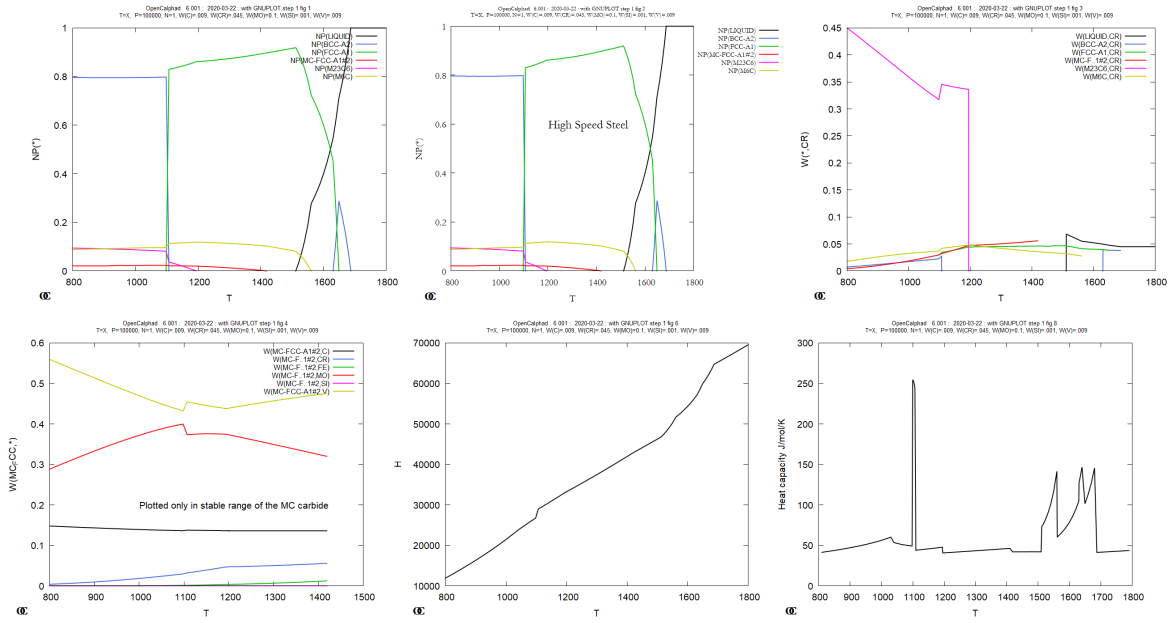
Macro file step1.OCM

A similar steel like in the example 4.1.3 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.



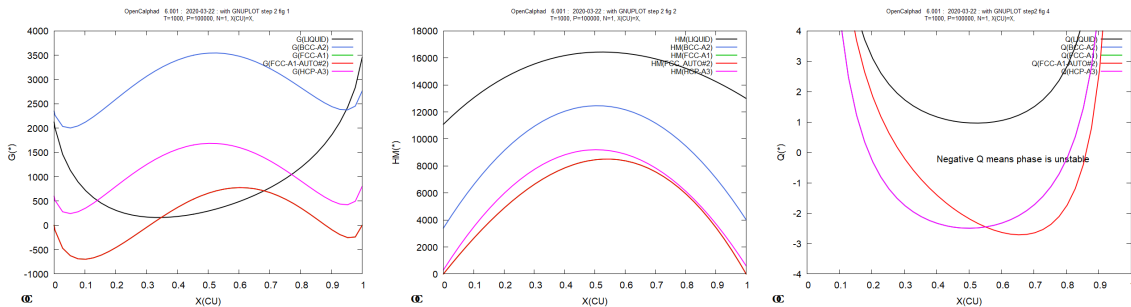


For plotting the GNUPLLOT software is used. The OC interface to GNUPLLOT uses only a minimum of the extensive facilities of GNUPLLOT. The first two plots is how the amount (in moles) of the phases varies with  $T$ . The next plot show the Cr content in the stable phases, then a plot of the composition of the cubic MC carbide, then the enthalpy variation with  $T$  and finally we have entered 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 in the diagram.

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

Macro file step2.OCM

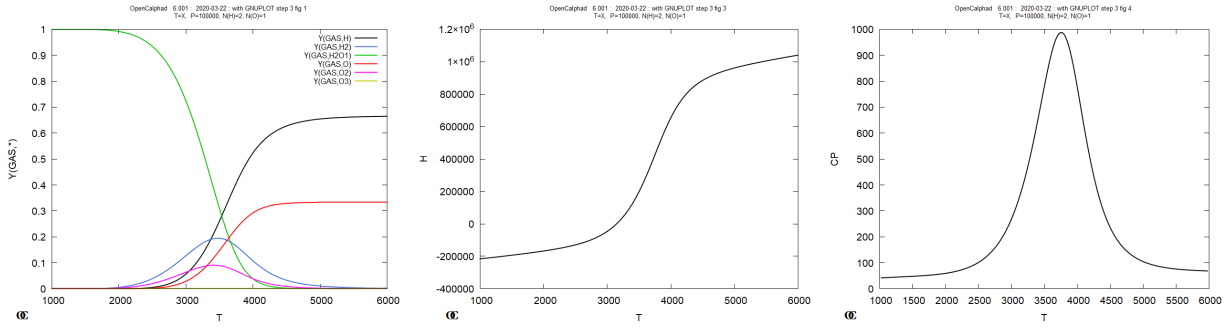
This was my first calculation of Gibbs energy curves with OC so I have kept it. In the middle diagram the enthalpy is plotted and in the right hand diagram the lowest eigenvalue of the Darken stability function, see 4.1.2, called  $Q(\text{phase})$  is plotted. When this is negative the phase is inside the spinodal.



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

Macro file step3.OCM

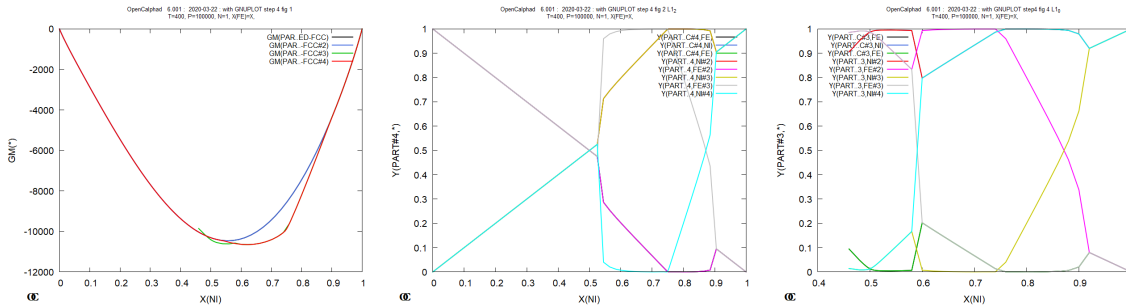
This calculates the speciation of  $\text{H}_2\text{O}$  in a gas phase between 1000 and 6000 K. At low  $T$  the system consists of just the  $\text{H}_2\text{O}$  molecule but around 2000 K this splits up in several molecules and above 5000 K only atomic H and O are present. This changes the configurational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



### 4.2.4 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 how the Gibbs energy curves and sublattice occupancy, i.e. constitution varies with composition. The ordered forms are not stable across the whole composition range.

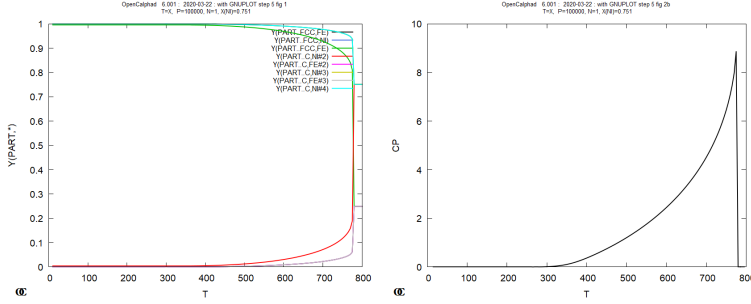


After calculating these diagram the macro uses the command **calculate phase ... const\_adj** to show that this command can calculate the ordering for a single phase giving the overall composition.

#### 4.2.5 Diagrams for constitution and heat capacity for DFT calculated ordered FCC in Fe-Ni at $\text{Ni}_3\text{Fe}$

Macro file step5.OCM

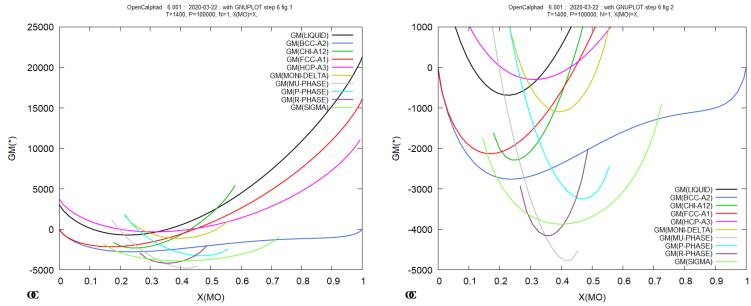
The same DFT data used for a fixed composition  $\text{FeNi}_3$  to calculate the constituent fractions for varying  $T$  and their contribution to the heat capacity.



#### 4.2.6 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.

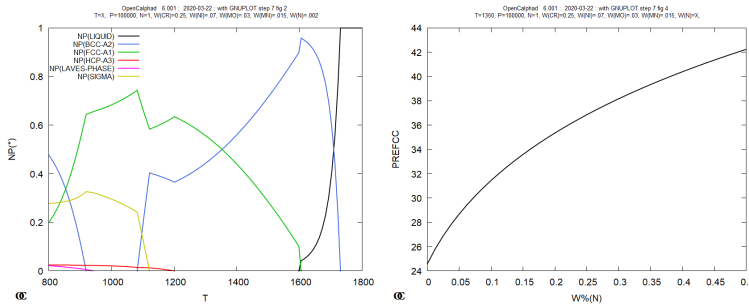


The right hand figure is a magnification.

#### 4.2.7 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.

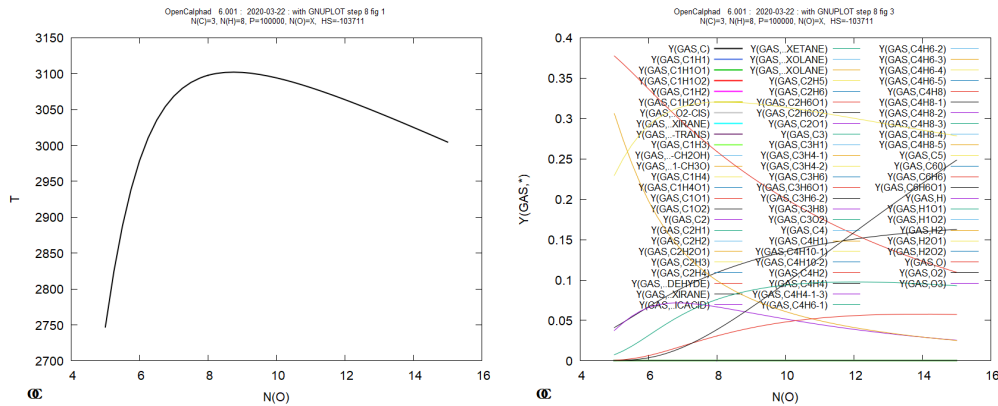


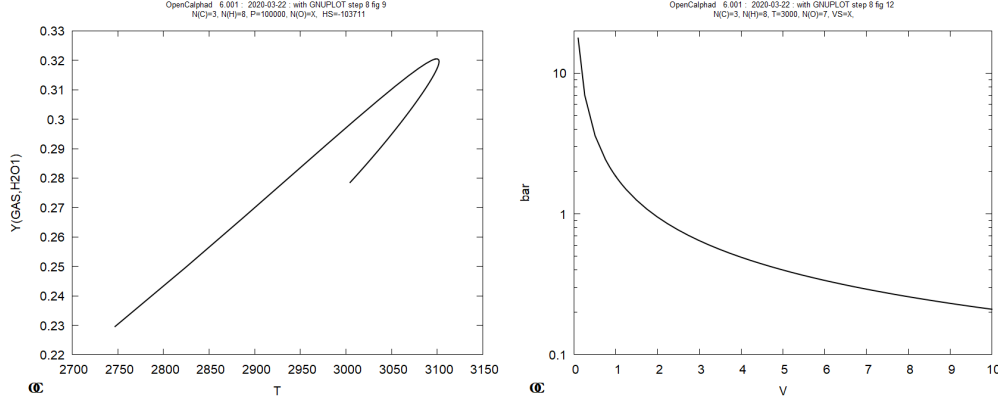
In the right hand figure we have plotted the PRE for FCC defined by the function:  
ent sym prefcc=100\*w(fcc,cr)+300\*w(fcc,mo)+1600\*w(fcc,n);

#### 4.2.8 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 propane ( $C_3H_8$ ) 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.





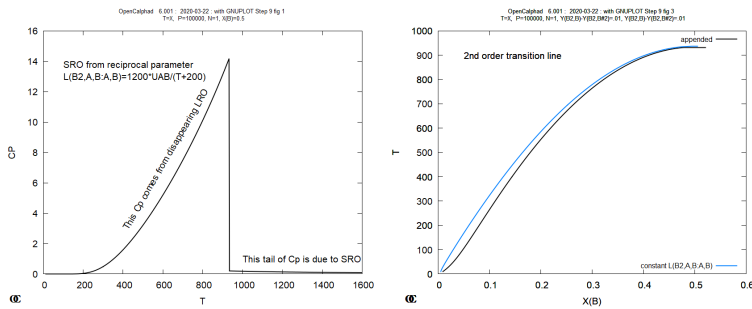
In the first diagram above the fraction the value of the  $T$  as function of moles of oxygen for one mole of propan. In the second diagram how the fraction of different gas species varies with the oxygen content and in the third figure how the fraction of  $H_2O$  species varies as function of  $T$ . All figures plotted from the same STEP calculation.

After these diagrams the oxygen amount set as a condition and the pressure,  $P$  is allowed to vary to calculate P-V diagram for the system in the last diagram using a logarithmic scaling on the Y axis. We can find that Boyle's law,  $PV = NRT$  is not valid for this gas because there are reactions between the constituents, the fraction of larger molecules increase with  $P$ .

#### 4.2.9 Long and short range ordering model for B2

Macro file step9.OCM

This is testing a model for adding SRO to the CEF model for LRO. The reciprocal parameter which gives a reasonable contribution to the Gibbs energy describing LRO has been made  $T$  dependent to also give a contribution to the heat capacity. This has a small influence on the 2nd order transition at low  $T$ .



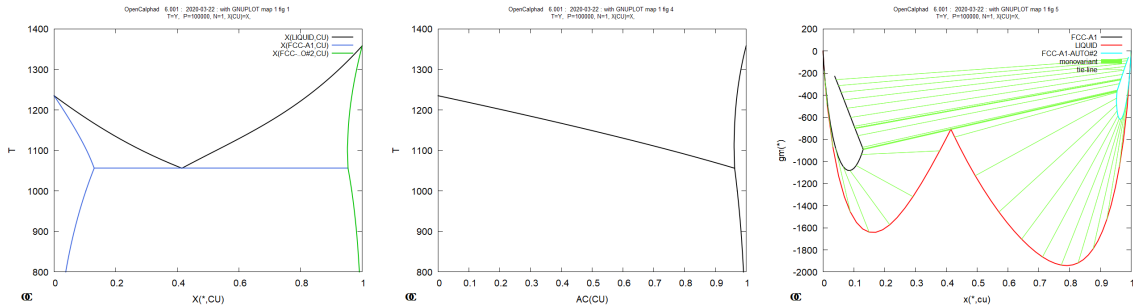
## 4.3 Phase diagram calculations

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

### 4.3.1 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. See section 4.2.2 for the Gibbs energy curves.



After a calculation One can plot the diagram with different ranges and axis variables, in the middle diagram the chemical potential of Cu is used instead of the fraction. The two-phase regions then becomes a line and the invariant eutectic a point where the lines meet. The rightmost diagram plot the Gibbs energies of the phases in equilibrium, the tie-lines connect the two phases in equilibrium. The three-phase equilibrium is a straight line because the chemical potentials of the elements are the same in all three phases.

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

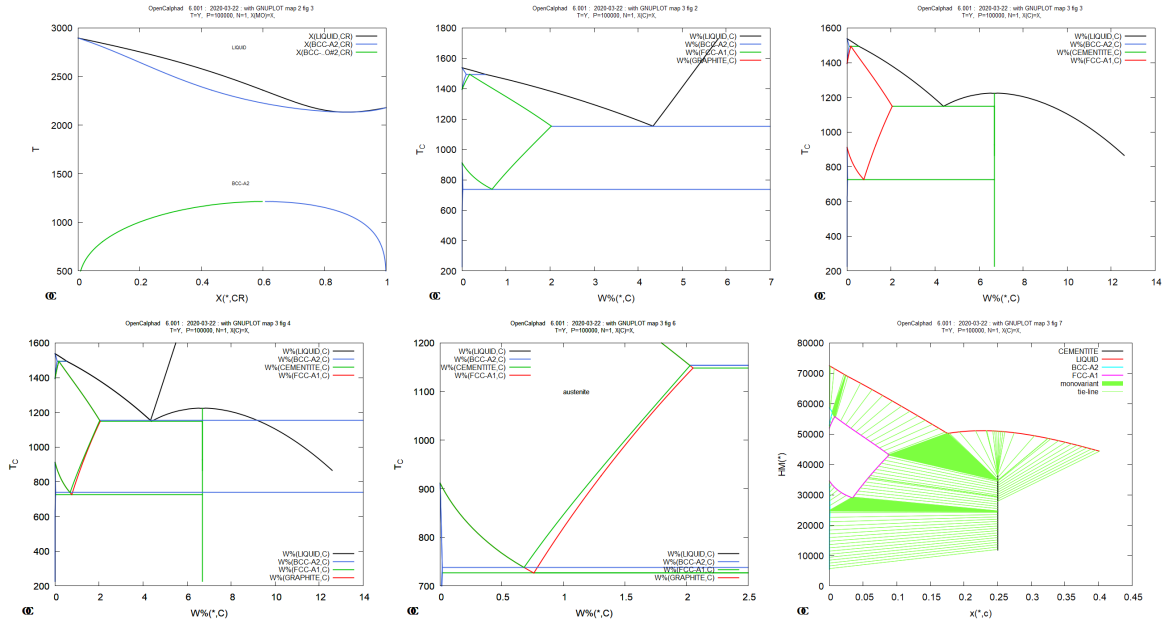
Macro file map2.OCM

There is a miscibility gap in the BCC phase also in the Cr-Mo system. The phase diagram is shown below. 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.

### 4.3.3 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.

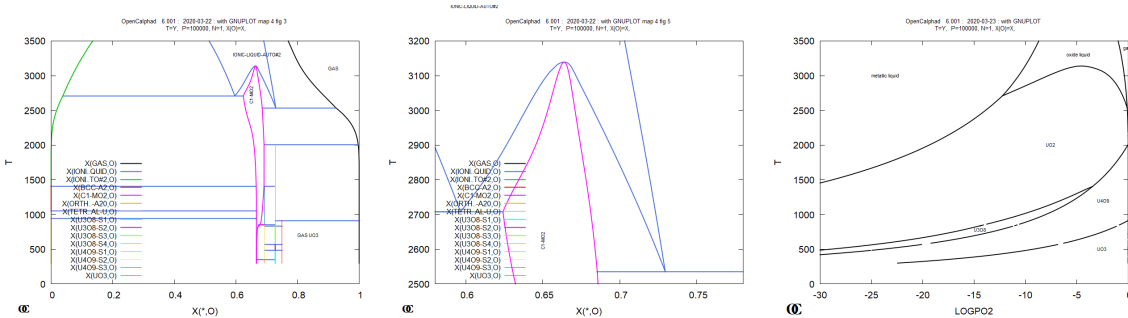


The first diagram is for map2. The next diagram is the stable Fe-C phase diagram with graphite. In the third diagram it is the metastable diagram with cementite. In the next diagram on the next row the two calculations are overlayed up to 7% C per weight. In the middle diagram the austenite region is magnified. 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. In the last diagram we change the vertical axis to the enthalpy content of each phase, the tie-lines connect the phases in equilibrium. The three phase equilibria are now mononariant areas.

#### 4.3.4 Phase diagram for O-U

Macro file map4.OCM

The phase diagram for O-U can now be calculated almost without problems although the step length control is not very good.



The middle diagram is a magnification of the congruent melting and the right hand plot has the oxygen potential as  $\log(p_{O_2})$  as the horizontal axis. The gaps are due to missing

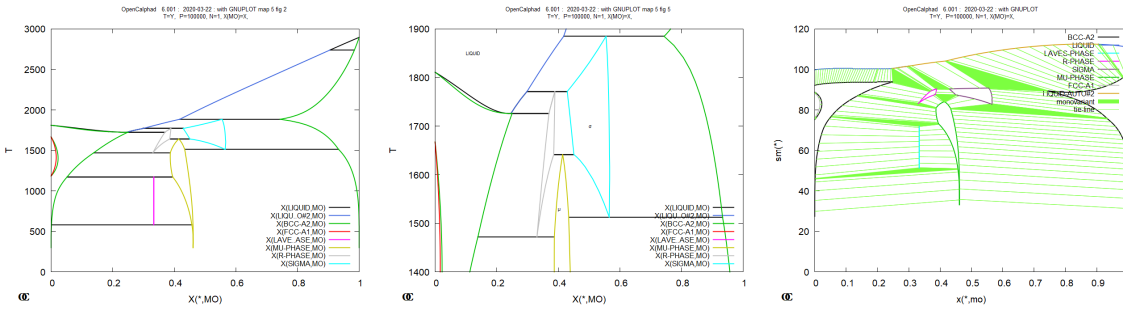
horizontal lines where the stoichiometric phases change structure.

The macro shows also how to calculate the congruent melting point exactly.

### 4.3.5 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 middle shows that with some GNUPLLOT drivers one can use greek letters. In the right hand diagram we plot the entropy in the phases vs composition.

### 4.3.6 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. The diagram is in the next section.

### 4.3.7 Isopleth calculation of a HSS

Macro file map7.OCM

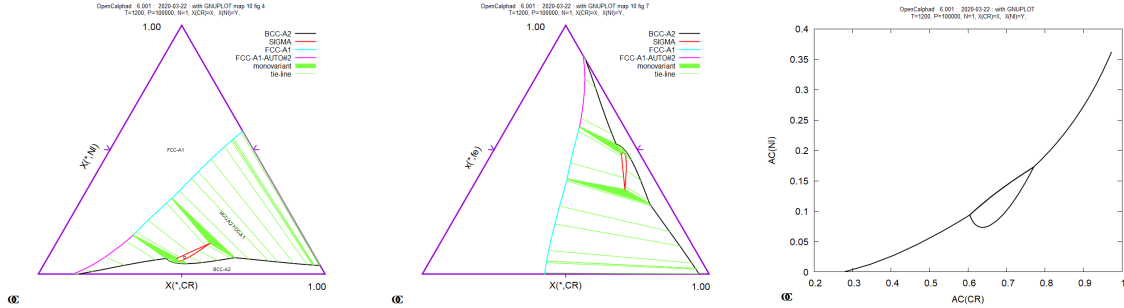
The phase diagram for this 6 component High Speed Steel (HSS) in the middle below is now almost correct and the phase labels show the stable phases in various regions. The check at the node points if the equilibrium is global has removed all metastable lines. But some lines are still missing and a better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





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 when both axis variables are extensive variables. Note one can write text with a slope and shift axis variables. The final diagram use potentials and the two-phase regions are a single line and the odd bubble in the middle is the sigma phase.

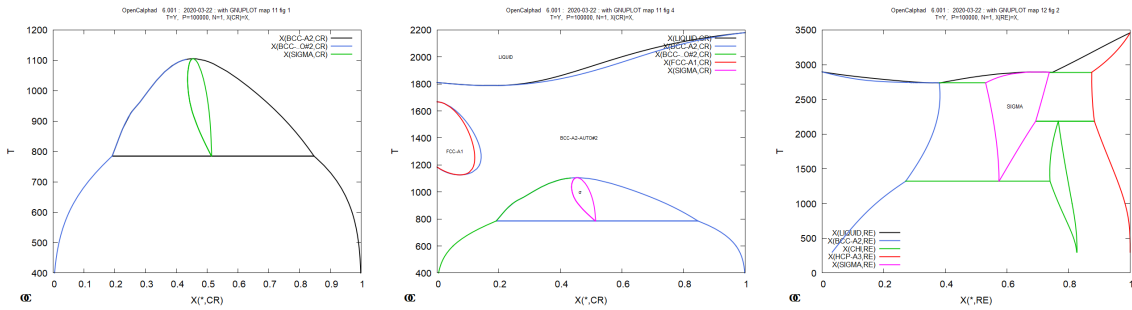


#### 4.3.11 The binary Cr-Fe phase diagram

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 and thus three start points are needed to calculate this diagram.



#### 4.3.12 The binary Mo-Re phase diagram

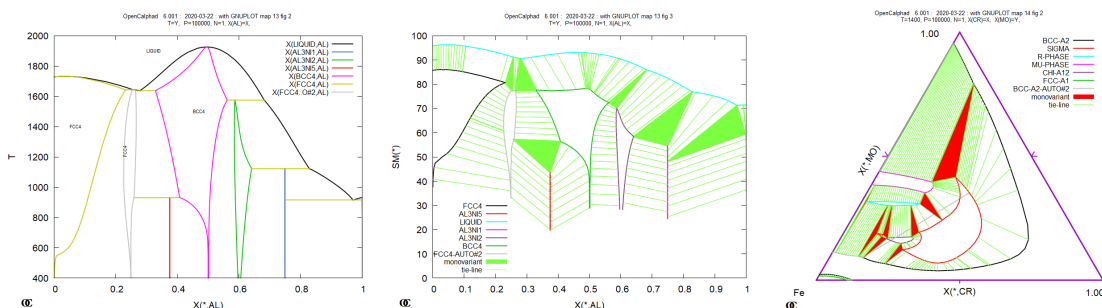
Macro file map12.OCM

This is just a test reading a database in the PDB format. The diagram is shown above.

### 4.3.13 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. The right hand diagram use the entropy of the phases instead of  $T$  as vertical axis. Note that “Richard’s rule” is not valid for compounds.



### 4.3.14 The Cr-Fe-Mo isothermal phase diagram

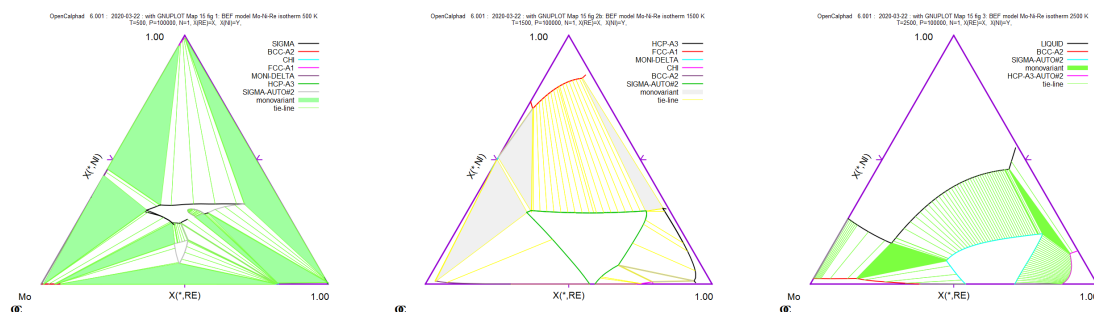
Macro file map14.OCM

This phase diagram has several intermetallic phases stable at 1400 K in the Cr-Fe-Mo system, the diagram is shown above. There are sometimes spurious jumps and the distances between the tie-lines are quite varied. The color of the monovariant areas can be set by the user and one can put a short text in the left hand corner. Triangular diagrams are still primitive and scaling ticks are missing.

### 4.3.15 The ternary Mo-Ni-Re using the BEF model

Macro file map15.OCM

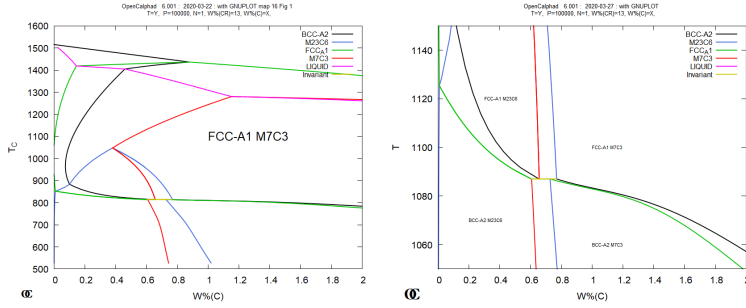
The Bond Energy Formalism has been used to model the phases in the Mo-Ni-Re system and 3 isothermal section has been calculated at 500, 1500 and 2500 K as shown below.



#### 4.3.16 The ternary isopleth in C-Cr-Fe system

Macro file map16.OCM

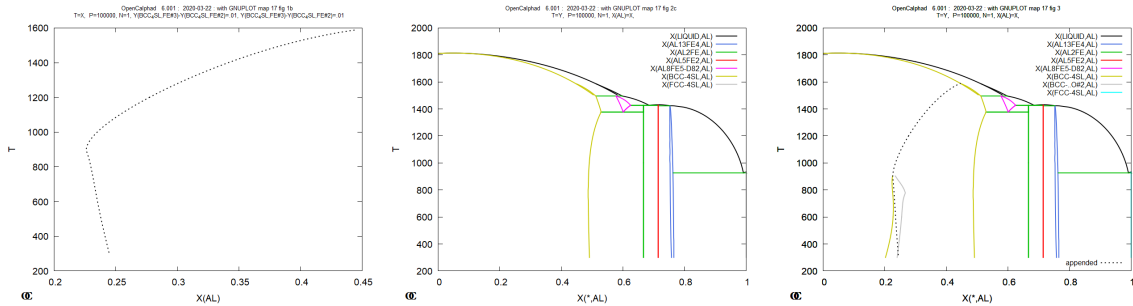
The ternary isopleth for Fe-13%Cr-C (in weight) is calculated and plotted below. There is a short invariant 4 phase equilibrium at 1087 K (814 °C) between BCC/FCC/M7C3/M23C6.



#### 4.3.17 The binary Al-Fe phase diagram

Macro file map17.OCM

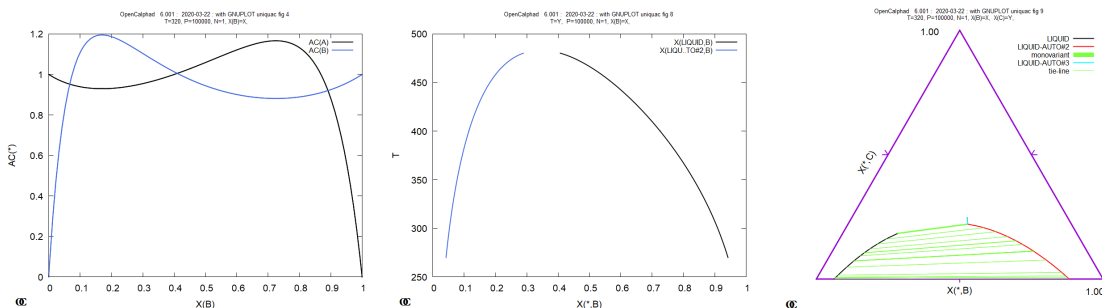
The models used for this diagram include a 4 sublattice model for the BCC-A2 phase to handle the B2 and D0<sub>3</sub> ordering. The magnetic ordering does also complicate the modeling. In the first figure the 2nd order transition between A2/B2 or D0<sub>3</sub> is plotted as dashed. In the middle diagram the liquid and various solid phases has been calculated. Finally in the right hand figure we combine these together with the first order transition between A2/B2 or D0<sub>3</sub> at low  $T$ .



#### 4.3.18 The UNIQUAC model

Macro file uniquac.OCM

The UNIQUAC model for polymeric liquids at ambient  $T$  has been implemented in OC [20Li]. It has a strongly non-ideal configurational entropy depending on the size of the molecules. Some diagrams calculated using this model are shown below. The mapping has problems with the closing of miscibility gaps.



## 4.4 Miscellaneous calculations, assessments, parallel etc

This section contains various examples.

### 4.4.1 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.

### 4.4.2 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.

### 4.4.3 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.

### 4.4.4 Setup of an assessment with fictitious binary experimental data

Macro file opttest1.OCM

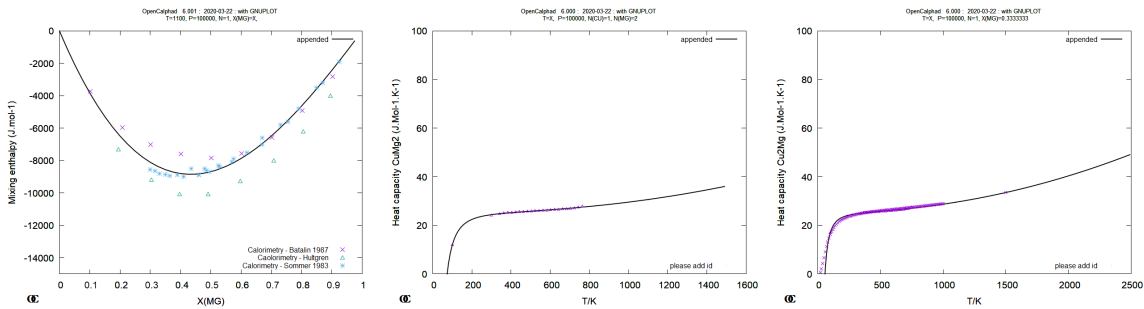
A tentative start of an assessment of a phase in a binary system. It shows how to enter experimental data and optimizing coefficients and how the weighting can change the results. It also shows how results from one equilibrium can be transferred to another.

#### 4.4.5 Start of an assessment of the Cu-Mg binary system

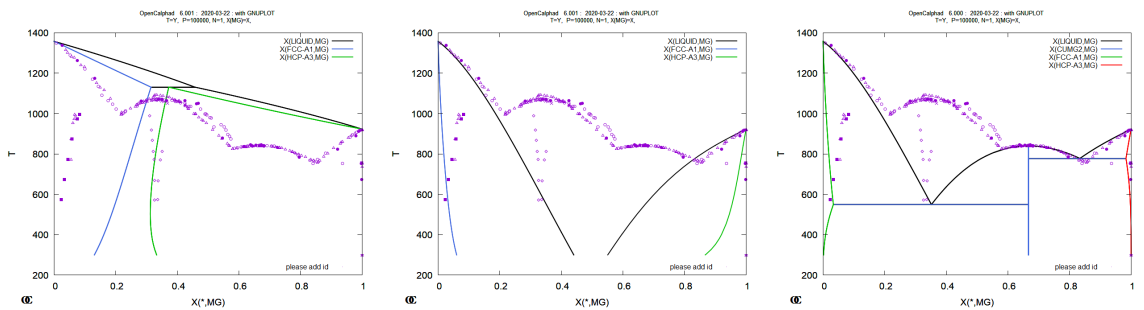
Macro file opttest2.OCM

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 first row of diagrams below the enthalpy of mixing in the liquid has been fitted and plotted together with experimental data and then the heat capacities for the two compounds.

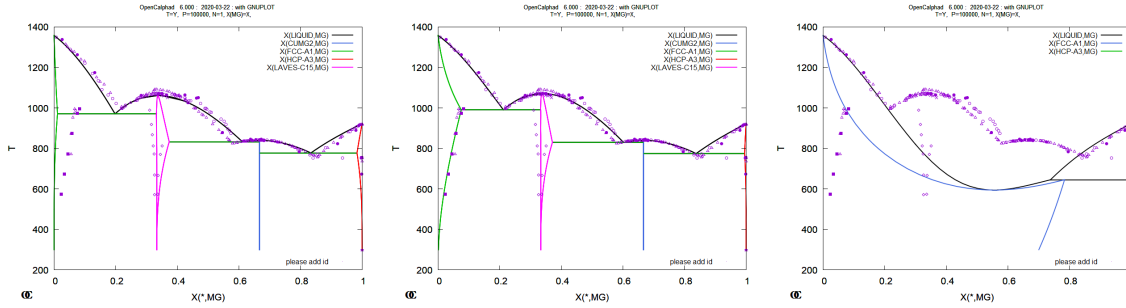


The remaining data on enthalpies, chemical potentials and the phase diagram are fitted step by step and the phase diagram develops as shown in the figures below. The first diagram below is with all solutions ideal and no parameters for the intermediate phases, the second after liquid enthalpy has been assessed and its negative enthalpy makes it more stable than the solid solutions at low  $T$ . In the rightmost diagram the  $Mg_2Cu$  compound has been fitted.



In the first diagram in the next set the Laves phase has been fitted and in the middle the solubilities in the FCC and HCP phases. The last diagram shows a metastable phase diagram without the intermediate phases, compare with the first two in the previous row!

The example does not make a total fit to all data, that is left to the user.



The SAVE facility, see example 4.1.4, 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.

## 5 Summary

Have fun and help make OC better!

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