OpenCalphad
Thermodynamics for Phase Diagrams and Simulations

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The regular solution

The classic model in Calphad is the substitutional regular solution phase assuming ideal configurational entropy:

$$G_M = \sum_i x_i \, {}^{\circ}G_i + RT \sum_i x_i \ln(x_i) + {}^{E}G_M \tag{1}$$

where x_i is the mole fraction of component i, ${}^{\circ}G_i$ the Gibbs energy of component i relative to the reference state for i i.e. the lattice stability.
The excess Gibbs energy ${}^{E}G_M$ is a sum of binary and higher order interactions:

$$\begin{aligned}
{}^{E}G_M &= \sum_i x_i \sum_{j>i} x_j (L_{ij} + \sum_{k>j} x_k (L_{ijk} + \cdots)) && (2)\\
L_{ij} &= \sum_{\nu=0}^{n} (x_i - x_j)^{\nu} \cdot {}^{\nu}L_{ij} && (3)\\
L_{ijk} &= v_i \, {}^{i}L_{ijk} + v_j \, {}^{j}L_{ijk} + v_k \, {}^{k}L_{ijk} && (4)\\
v_i &= x_i + (1 - x_i - x_j - x_k)/3 && (5)
\end{aligned}$$

where the binary and ternary interactions can be composition dependent and ${}^{\nu}L_{ij}$ and ${}^{i}L_{ijk}$ can be linearly T dependent.

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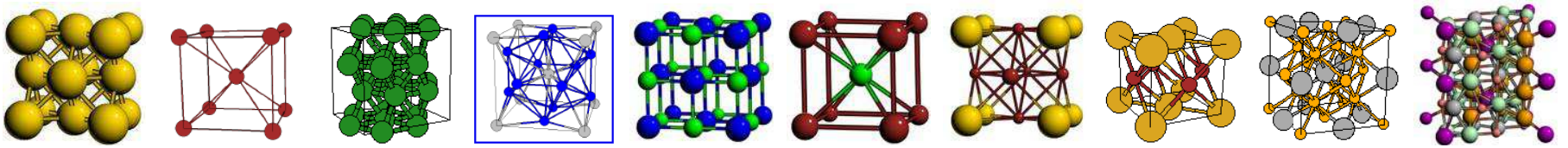
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where the binary and ternary interactions can be composition dependent and ${}^{\nu}L_{ij}$ and ${}^{i}L_{ijk}$ can be linearly T dependent.
The weak point in this model is the ideal configurational entropy and the first step to improve the modeling for solid phases is to include Long Range Ordering (LRO).

The Compound Energy Formalism (CEF)

The regular solution model cannot be used for solid crystalline phases with many sublattices:



A1 A2 A3 A15 B1 B2 $L1_2$ $L1_0$ $D0_3$ $D8_b$

The Compound Energy Formalism (CEF) include LRO in the generic Gibbs energy function for phase α:

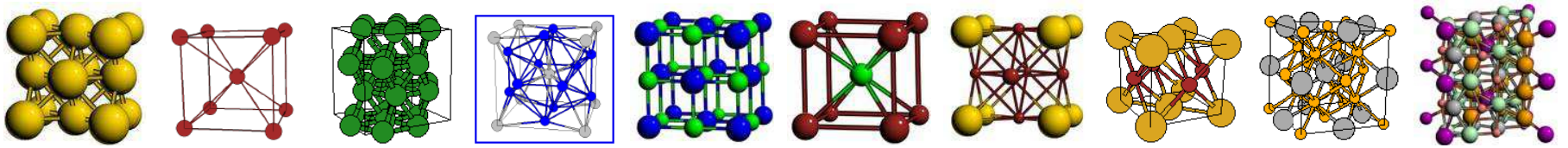
$$G_M^\alpha = {}^{\mathrm{srf}}G_M^\alpha + RT\sum_s a_s \sum_i y_{si} \ln(y_{si}) + {}^{E}G_m^\alpha + {}^{\mathrm{phys}}G_M^\alpha \quad (6)$$

$${}^{\mathrm{srf}}G_M^\alpha = \sum_I P_I(Y) \, {}^{\circ}G_I^\alpha \quad (7)$$

where ${}^{\mathrm{srf}}G_M$ is the surface of reference depending on the Gibbs energies, ${}^{\circ}G_I$, of the endmembers I with one constituent in each sublattice relative to the reference state for the elements. The endmembers are compounds that often can be calculated by DFT.
$P_I(Y)$ is the product of the constituent fractions defined by I and y_{si} is the fraction of constituent i in sublattice s. a_s is the number of sites in sublattice s.

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$P_I(Y)$ is the product of the constituent fractions defined by I and y_{si} is the fraction of constituent i in sublattice s. a_s is the number of sites in sublattice s.
${}^{E}G_M^\alpha$ is the excess Gibbs energy with interaction parameters are similar to those used in the regular model with two or more constituents in one or more sublattices.
${}^{\mathrm{phys}}G_M^\alpha$ is the contribution from particular physical phenomena such as magnetism.
Note the Gibbs energy, G_M, is defined per mole formula unit as the model may include vacancies.

The reciprocal model

CEF contains many models as subsets and the important one is the reciprocal model which has two sublattices and two constituents in each. It can be written as

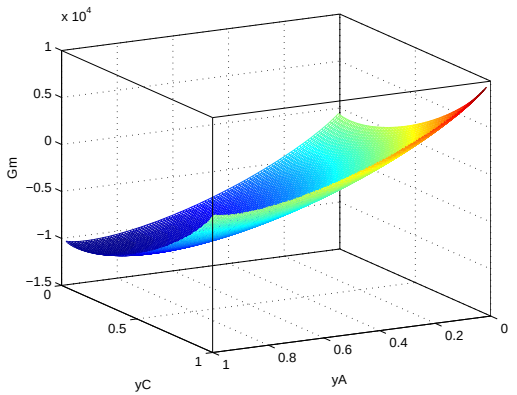
$$(\mathrm{A,B})_a(\mathrm{C,D})_c$$

where A and B are constituents on the first sublattice and C and D are constituents on the second and a and c are stoichiometric factors. This is the simplest model describing LRO and it has many interesting properties.

It is called reciprocal because there is a relation between the 4 endmember energies:

$$\Delta G \quad = \quad {}^{\circ}G_{A:C} + {}^{\circ}G_{B:D} - ({}^{\circ}G_{A:D} + {}^{\circ}G_{B:C}) \qquad (8)$$

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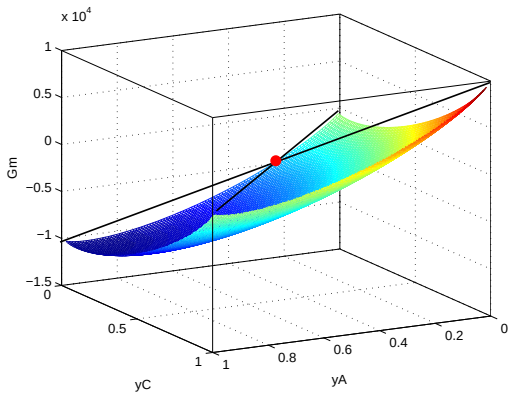
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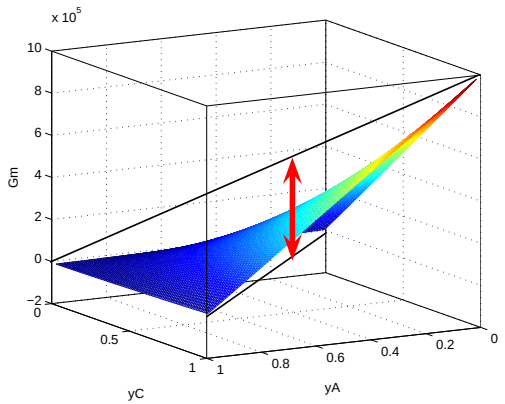
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With a $\Delta G \neq 0$ as here, drawn by a red arrow, we may have a miscibility gap. .



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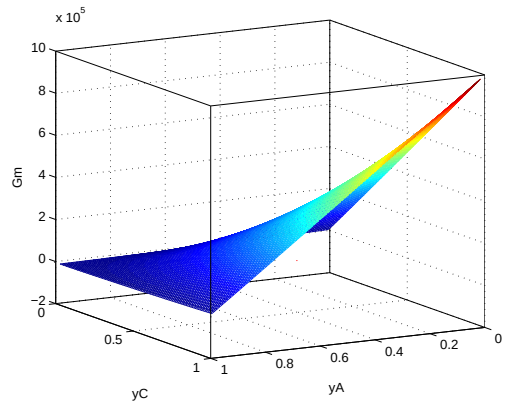
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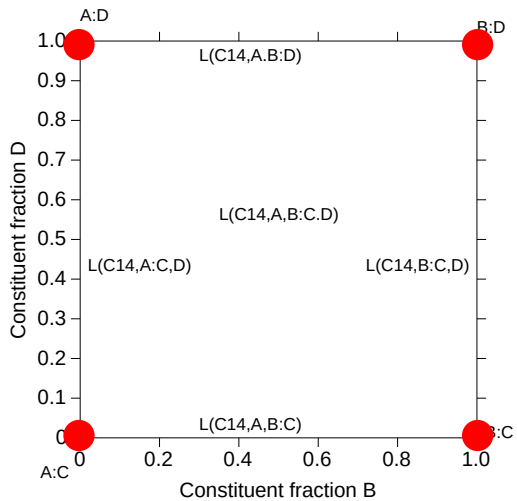
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This square represents the constitutional space in the system with an endmember at each corner. There are 4 excess parameters representing interactions along the edges of the system and a new reciprocal parameter $L_{\mathrm{A,B:C,D}}$ representing an exchange interaction on both sublattices.



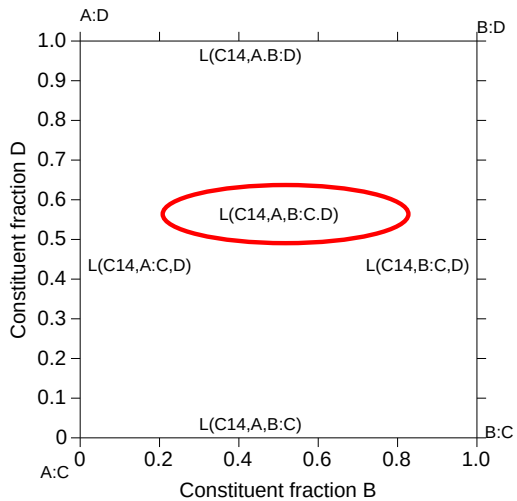
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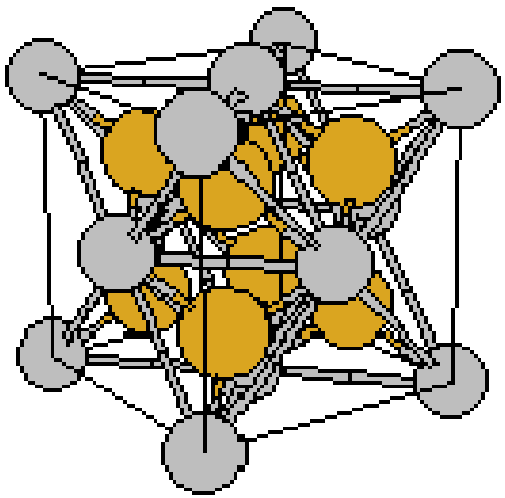


The reciprocal interaction parameter in the center turns out to be very important as it can be used to approximate the contribution from SRO in systems with order/disorder transitions. CEF models with more sublattices and constituents can always be reduced to a number of reciprocal subsystems which can give important relations between the endmembers.

Modeling defects with CEF

The UO_2 phase has a C1 structure. Uranium (gray) occupies the FCC lattice and oxygen (orange) the tetrahedral interstitial sites. Uranium can have $+3$, $+4$ and $+5$ charges, oxygen always -2. The composition can vary by vacancies on the oxygen sublattice and oxygen on the octahedral interstitial sites. This gives a CEF model:

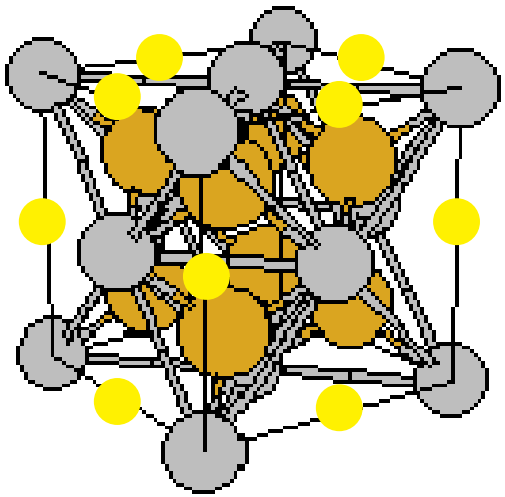
$$(\mathrm{U}^{+3}, \mathrm{U}^{+4}, \mathrm{U}^{+5})_1(\mathrm{O}^{-2}, \mathrm{Va})_2(\mathrm{O}^{-2}, \mathrm{Va})_1$$



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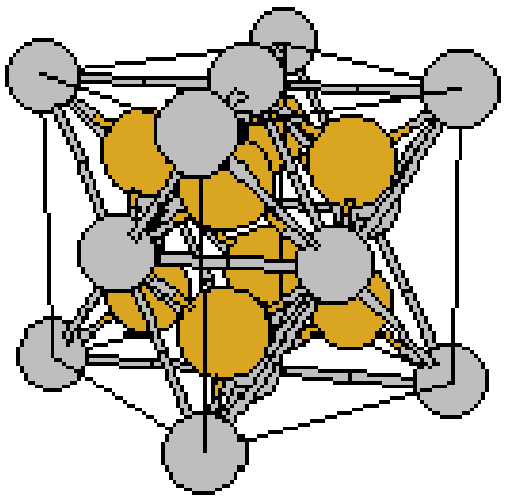


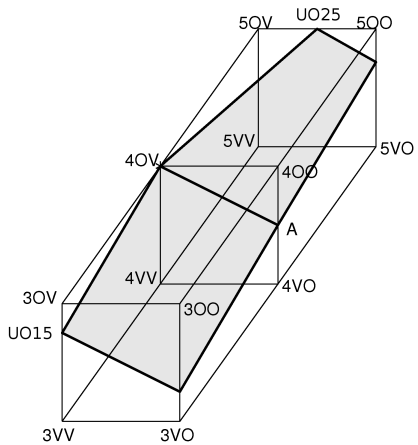
Some of the octahedral interstitial sites for oxygen are shown here as yellow dots.

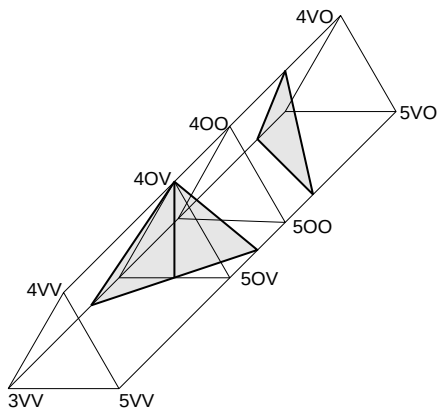
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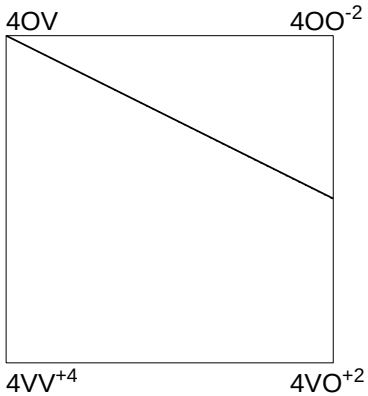
All endmembers (except one) has a net charge.
The shaded areas are electrically neutral

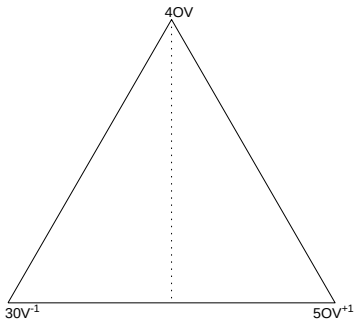
Figures like these two showing the geometrical relation between the endmembers can be useful to understand the relation between the 12 endmembers (only one of which is electrically neutral) in order to describe the very extensive thermodynamic data on the C1 phase.

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From the 3D prisms on the previous slide one can extract some more useful figures for well known types of defects:

This reciprocal square represent a Frenkel defect when an oxygen ion moves to an interstitial site.
This triangle represent a charge defect when $U^{+4} = 0.5U^{+3} + 0.5U^{+5}$





$$G^{\mathrm{Frenkel}} = 0.5(\,{}^{\circ}G_{\mathrm{U}^{+4}:\mathrm{Va}:\mathrm{O}^{-2}} + {}^{\circ}G_{\mathrm{U}^{+4}:\mathrm{O}^{-2}:\mathrm{O}^{-2}}) - {}^{\circ}G_{\mathrm{U}^{+4}:\mathrm{O}^{-2}:\mathrm{Va}} \quad (8)$$

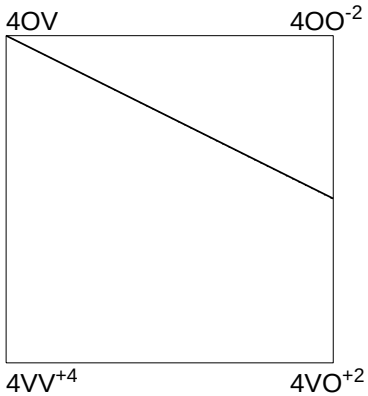
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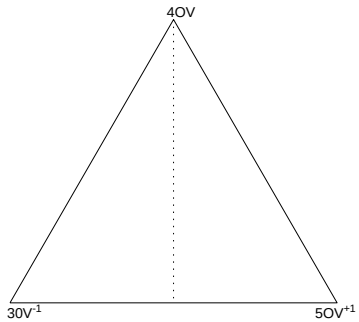
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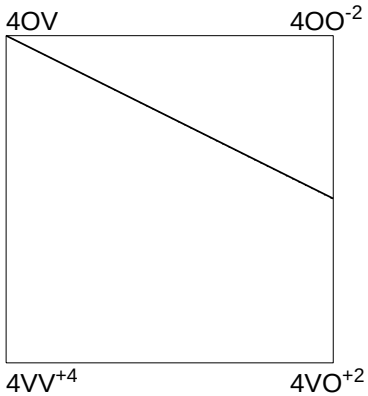
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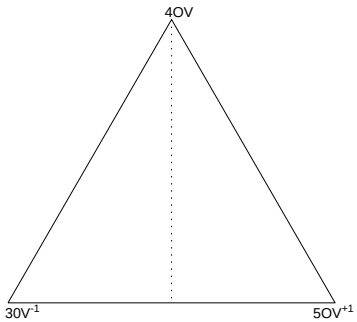
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This model can handle multiple defects and additions of any other element on the different sites. Inside a nuclear reactor you essentially have every element in the periodic chart.

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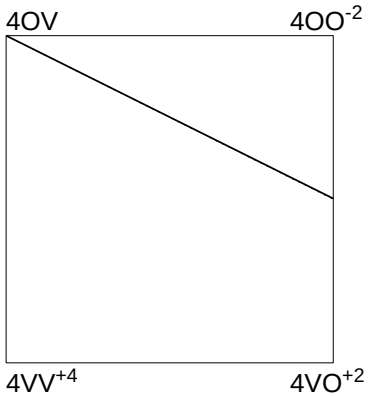
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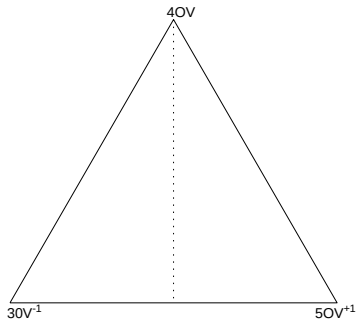
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A strength of the Calphad modeling of defects is the consistent method to model structures with multiple defects and high amount of defects.

Some steps in the development of thermodynamic models

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Some steps in the development of thermodynamic models

I was privileged to participate in the development of several models at the MSE department at KTH as a PhD student for Mats Hillert. In 1981 John Ågren and I wrote the classic paper on the sublattice model, now known as the Compound Energy Formalism (CEF).

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CVM developed by Kikuchi is the best model for SRO in phases with no LRO but CVM requires so many clusters that it is still too slow to be used for simulations for multi-component materials. For phases with LRO the contribution from SRO is small and can easily be included in the basic CEF model.

The disordered fraction set and EBEF

A phase with many sublattices and constituents will have many endmembers, a σ phase with 5 sublattices and 10 components has 10^5 endmembers. This is far less than the number of clusters using a CVM based model but anyway it is simply too many.
Commercial databases normally use only 3 sublattices for TCP phases such as σ. But a 10 component system with many TCP phases will anyway have to handle several 100 fraction variables to calculate the equilibrium.

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However, only a few of all possible endmembers in a TCP phase are important to describe the stable range of the phase because endmembers with a positive energy relative to a "mechanical mixture" of the components can be ignored. This has lead to the idea to introduce a *disordered fraction set* for phases with many sublattices:

$$(A,B,C,D,E,F)_2(A,B,C,D,E,F)_4(A,B,C,D,E,F)_8(A,B,C,D,E,F)_8(A,B,C,D,E,F)_8$$
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The configurational entropy is calculated using sublattices: $RT\sum_s a_s \sum_i y_{si} \ln(y_{si})$
The surface of reference, ${}^{\mathrm{srf}}G$, use the disordered set with the mole fractions $x_{\mathrm{A}} = \frac{\sum_s a_s y_{s,\mathrm{A}}}{\sum_s a_s}$.

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Only endmembers in the sublattice model with a Gibbs energy below the Gibbs energy surface defined by these two terms are needed to describe all possible stable states (the convex hull) of this phase.
Configurent independent interactions can also be introduced in the disordered fraction set.

The disordered fraction set and EBEF

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Phases with order/disorder transitions like FCC with the ordered superstructures $L1_2$, $L1_0$ require 4 sublattice but many of the endmembers have identical values, for example:
$^{\circ}G_{\mathrm{A:A:A:B}} = {}^{\circ}G_{\mathrm{A:A:B:A}} = {}^{\circ}G_{\mathrm{A:B:A:A}} = {}^{\circ}G_{\mathrm{B:A:A:A}}$

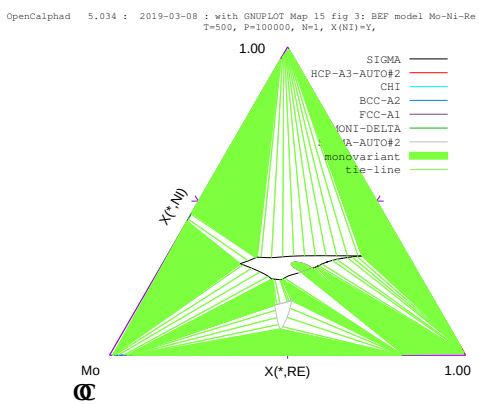
Considering this and including a disordered fraction set when designing the data structure for storing the parameters for such models simplifies database management and can speed up calculations.

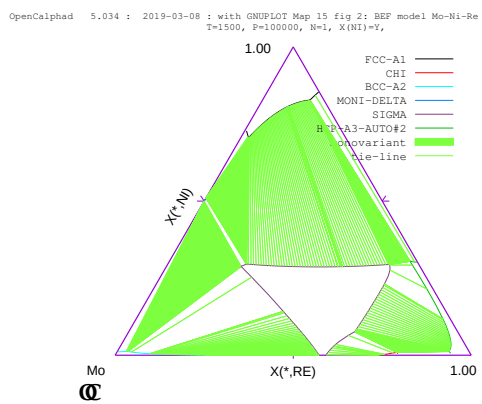
The disordered fraction set and EBEF

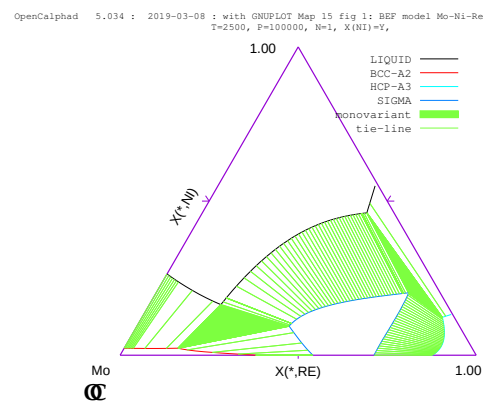
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A recent extension of CEF is to assume that the energy of the bond energy between atoms in different sublattices is independent of the constituents on the other sublattices i.e. using endmembers such as ${}^{\circ}G^{\sigma}_{\mathrm{A:B:*:*:*}}$, ${}^{\circ}G^{\sigma}_{\mathrm{*:A:B:*:*}}$ etc.

This Effective Bond Energy Formalism (EBEF) proposed by Nathalie Dupin can reduce the number of endmember parameters and seems to give better extrapolations to multi-component systems. The diagrams below are for the Mo-Ni-Re system at 500, 1500 and 2500 K where the stability range of the σ phase has a complex shape in competition with many other phases.







New thermodynamic models

Do we have the models we need
or those we deserve?

New thermodynamic models

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or those we deserve?

Although there is now a large repertoire of models for thermodynamics the quest for new models is not finished. There is usually no problem to fit known experimental and theoretical data in binary and ternary systems, the main challenge for the models is to **provide reliable extrapolations to multi-component systems**.

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High pressure data (several GPa) is also difficult to model. Partially because one has to use the Helmholtz energy rather than the Gibbs energy.

Data structures

- Structuring the static thermodynamic data
- Model parameter identifiers
- Structuring the dynamic equilibrium data

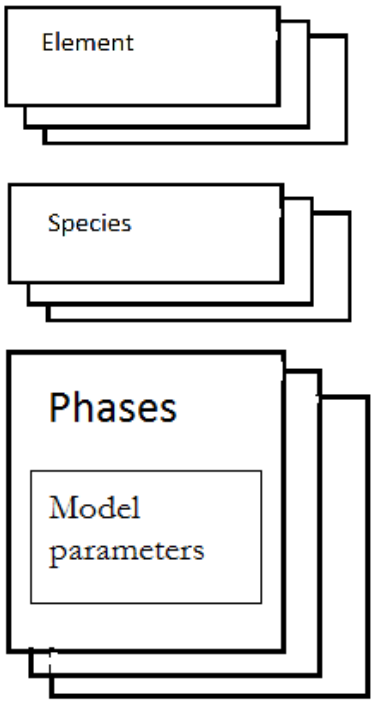
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Algorithms + Data Structures = Programs

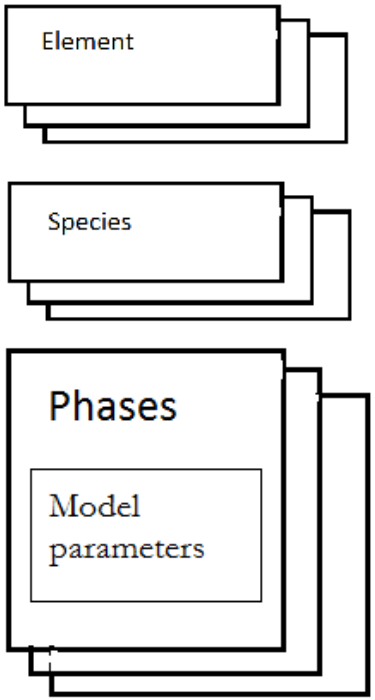
To use the thermodynamic models to calculate equilibria and thermodynamic properties we must implement then in a computer software.
Great care must be taken to handle multi-component systems and many different kinds of external conditions in an efficient way.

Static and dynamic data



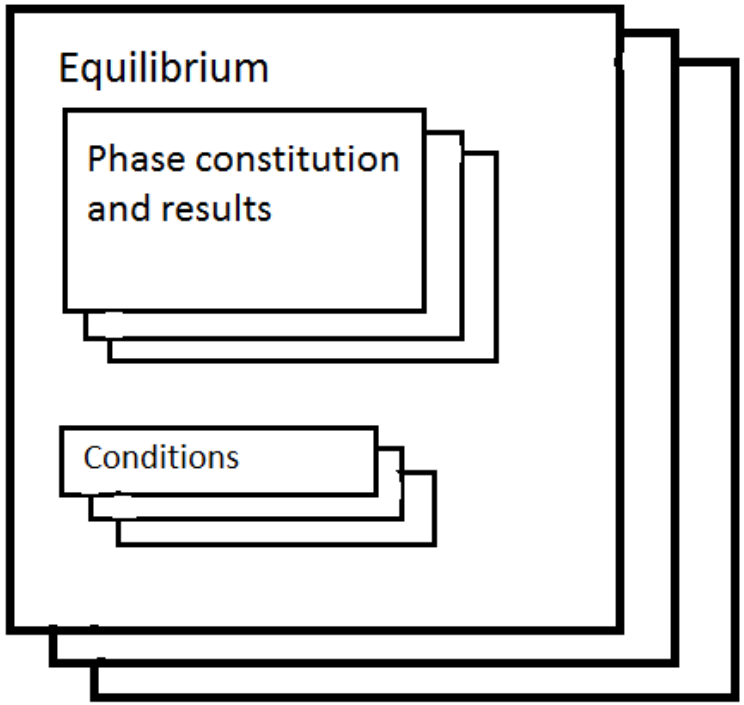
The data for elements, species and model parameters are independent on the external conditions on the system

Static and dynamic data



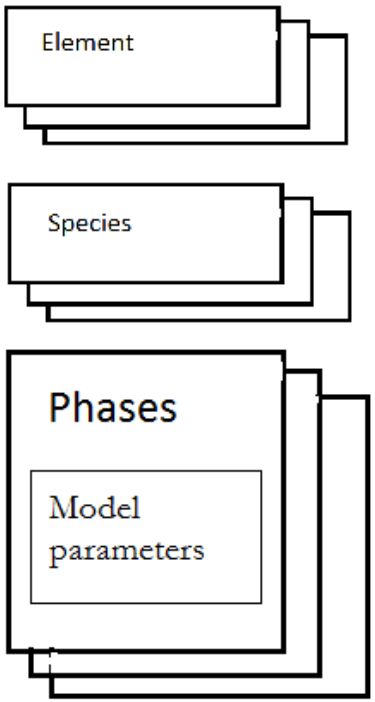
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Dynamic data

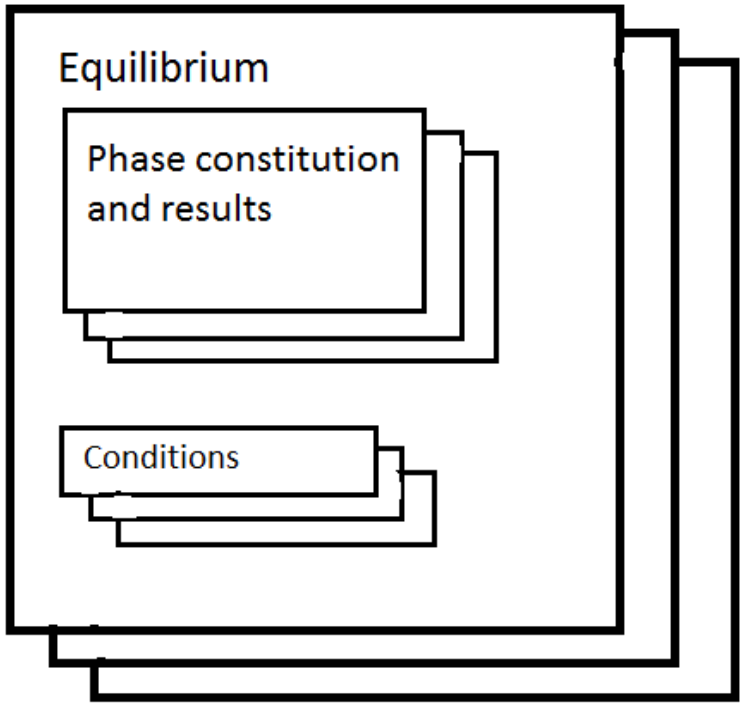


The amount and constitution of the phases vary with the external conditions like temperature and overall composition and are stored in the equilibrium record.

Static and dynamic data



Dynamic data

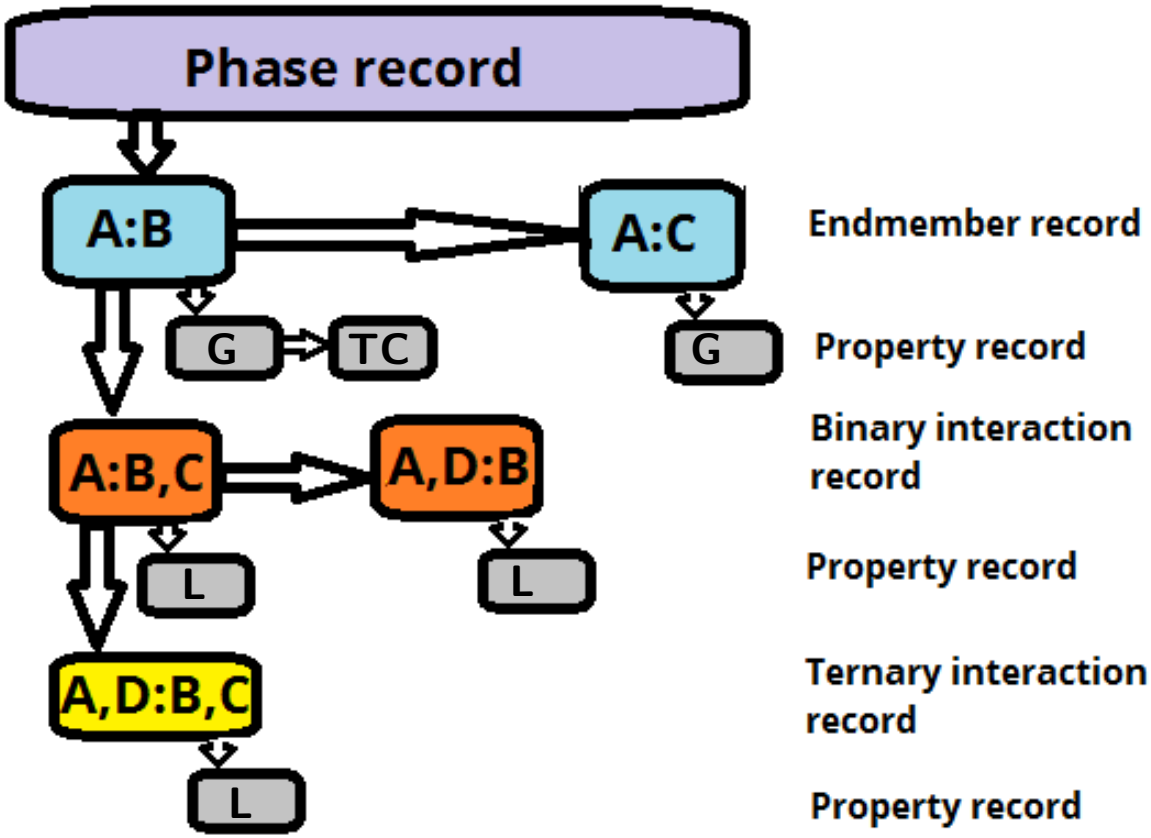


The data for elements, species and model parameters are independent on the external conditions on the system

In the dynamic data structure each equilibrium record has a separate set of conditions and results and they can be calculated in parallel.

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Static data, storing parameters for a phase $(A,D)_a(B,C)_b$



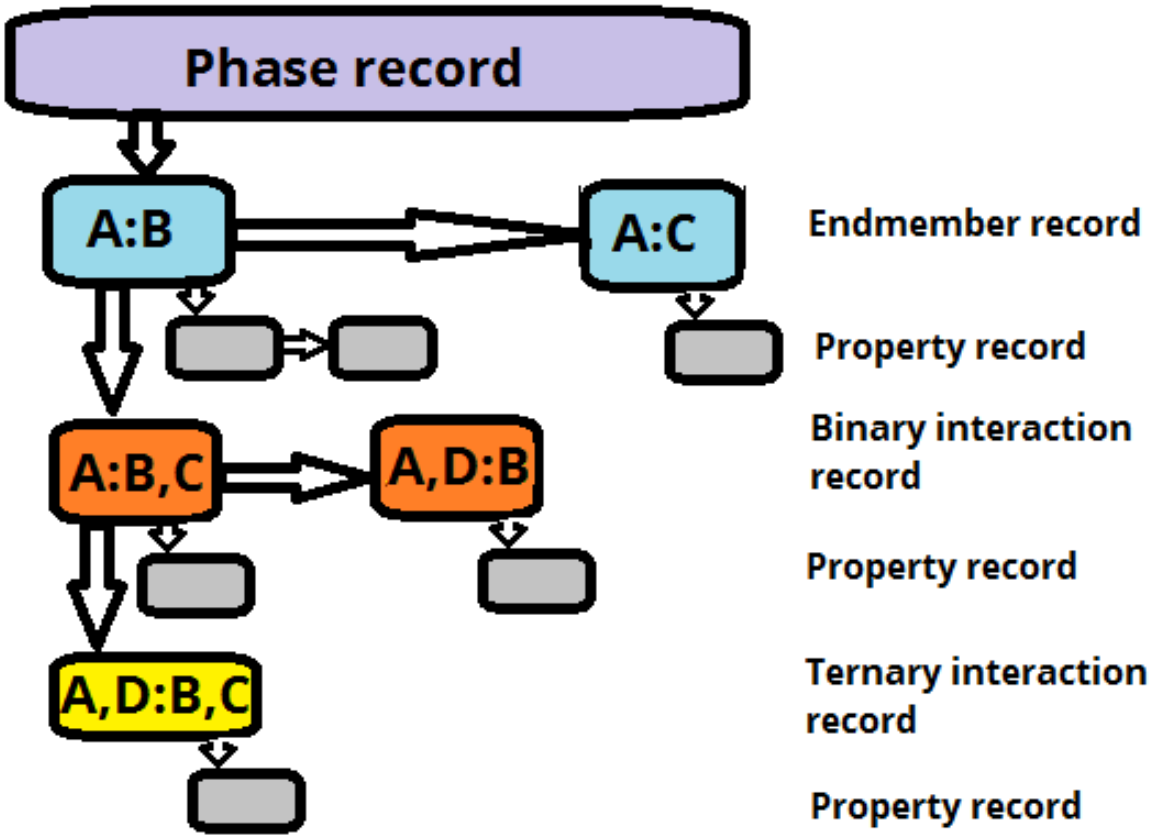
This data structure is a binary tree representing the Gibbs energy, G, and TC:

$$G = y_{1,\mathrm{A}} y_{2,\mathrm{B}} ({}^{\circ}G_{\mathrm{A:B}} + y_{2,\mathrm{C}} (L_{\mathrm{A:B,C}} + y_{1,\mathrm{D}} L_{\mathrm{A,D:B,C}}) + y_{1,\mathrm{D}} L_{\mathrm{A,D:B}}) + y_{1,\mathrm{A}} y_{2,\mathrm{C}} \, {}^{\circ}G_{\mathrm{A:C}}$$

$$TC = y_{1,\mathrm{A}} y_{2,\mathrm{B}} \, {}^{\circ}TC_{\mathrm{A:B}}$$

where the constituent fractions, y_{si} are stored in the dynamic data structure

Static data, storing parameters for a phase $(A,D)_a(B,C)_b$



The data structure can also be considered as a method to handle a sparse multi-dimensional matrix because the number of possible parameters can be very large in a multi-component phase with many sublattices.

Model property parameter identifiers

The method to describe the Gibbs energy used in the thermodynamic model can be extended to other properties which depend on the phase, the composition and T and P. In the OC data structure it is possible for a user to add parameters for many other phase dependent properties, also for properties can be useful for simulations, like atomic mobility, electric resistance, viscosity etc.

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Indx	Ident	T	P	Specification	Status	Note
1	G	T	P		0	Energy
2	TC	-	P		2	Combined Curie/Neel T
3	BMAG	-	-		1	Average Bohr magneton numb
4	CTA	-	P		2	Curie temperature
5	NTA	-	P		2	Neel temperature
6	IBM	-	P	&<constituent#sublattice>;	12	Individual Bohr magneton num
7	THET	-	P		2	Debye or Einstein temp
8	VO	-	-		1	Volume at T0, P0
9	VA	T	-		4	Thermal expansion
10	VB	T	P		0	Bulk modulus
11	G2	T	P		0	Liquid two state parameter
12	MQ	T	P	&<constituent#sublattice>;	10	Mobility activation energy
13	MF	T	P	&<constituent#sublattice>;	10	RT*ln(mobility freq.fact.)
14	MG	T	P	&<constituent#sublattice>;	10	Magnetic mobility factor
15	THT2	-	P		2	Smooth step function T
16	DCP2	-	P		2	Smooth step function value
17	VISC	T	P		0	Viscosity
18	LPX	T	P		0	Lattice param X axis
19	LPY	T	P		0	Lattice param Y axis
20	LPZ	T	P		0	Lattice param Z axis
21	LPTH	T	P		0	Lattice angle TH
22	EC11	T	P		0	Elastic const C11
23	EC12	T	P		0	Elastic const C12
24	EC44	T	P		0	Elastic const C44
26	UQT	T	P	&<constituent#sublattice>;	10	UNIQUAC residual parameter
25	RHO	T	P		0	Electric resistivity
26	LAMB	T	P		0	Thermal conductivity
27	TSCH	-	P		2	Schottky anomality T
28	CSCH	-	P		2	Schottky anomality Cp/R.

Dynamic data: Inside the equilibrium record 1



The equilibrium record contain all data that depend on the current set of conditions. This cupboard will be used as illustration.

Dynamic data: Inside the equilibrium record 1

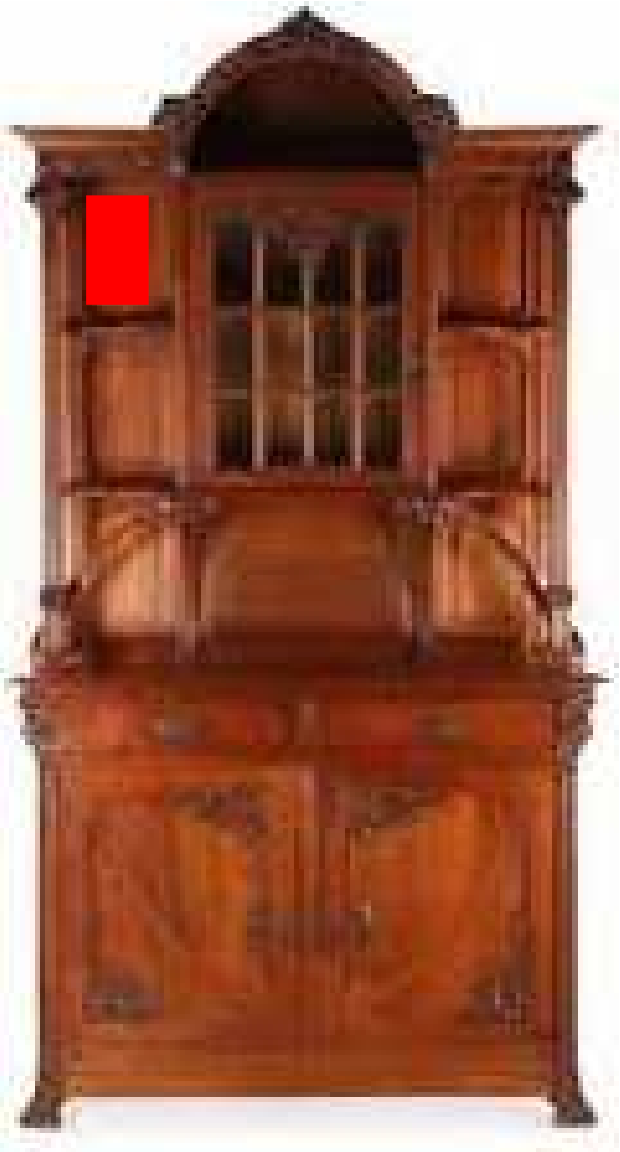


There are many of them so one can calculate equilibria in parallel. Each of them has a link to the same static data structure with the data for elements, phases and model parameters.

Dynamic data: Inside the equilibrium record 2



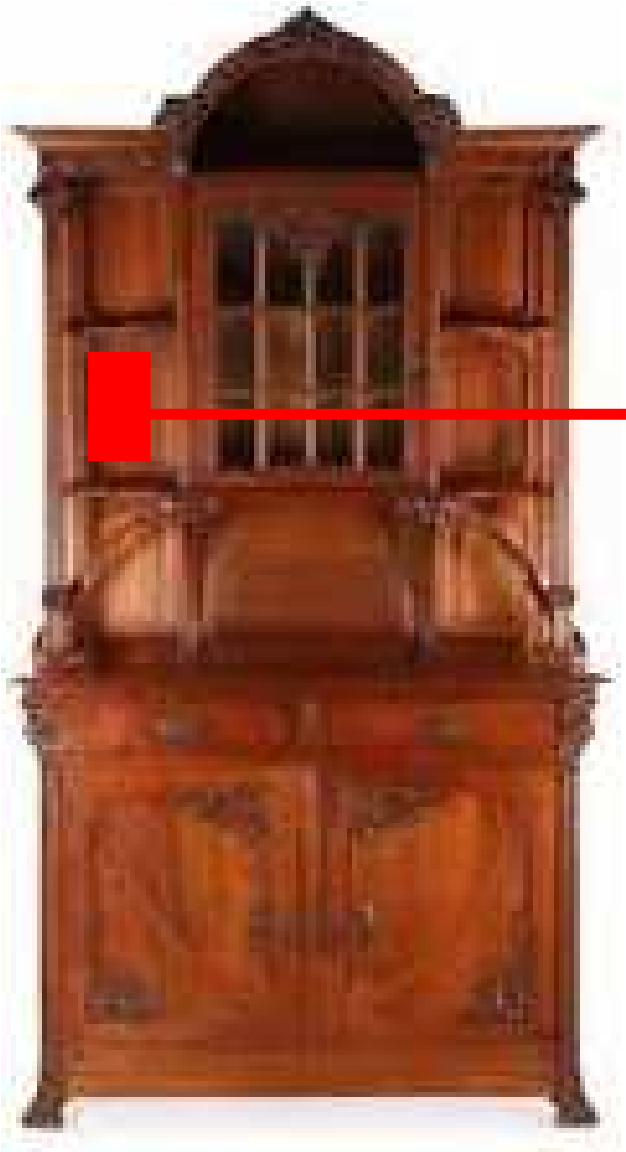
Dynamic data: Inside the equilibrium record 2



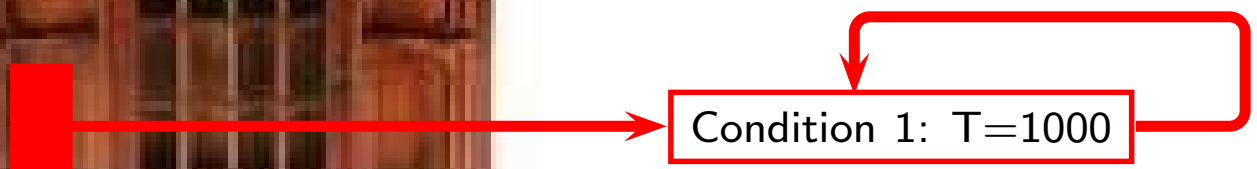
Name and index of equilibrium

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Dynamic data: Inside the equilibrium record 2

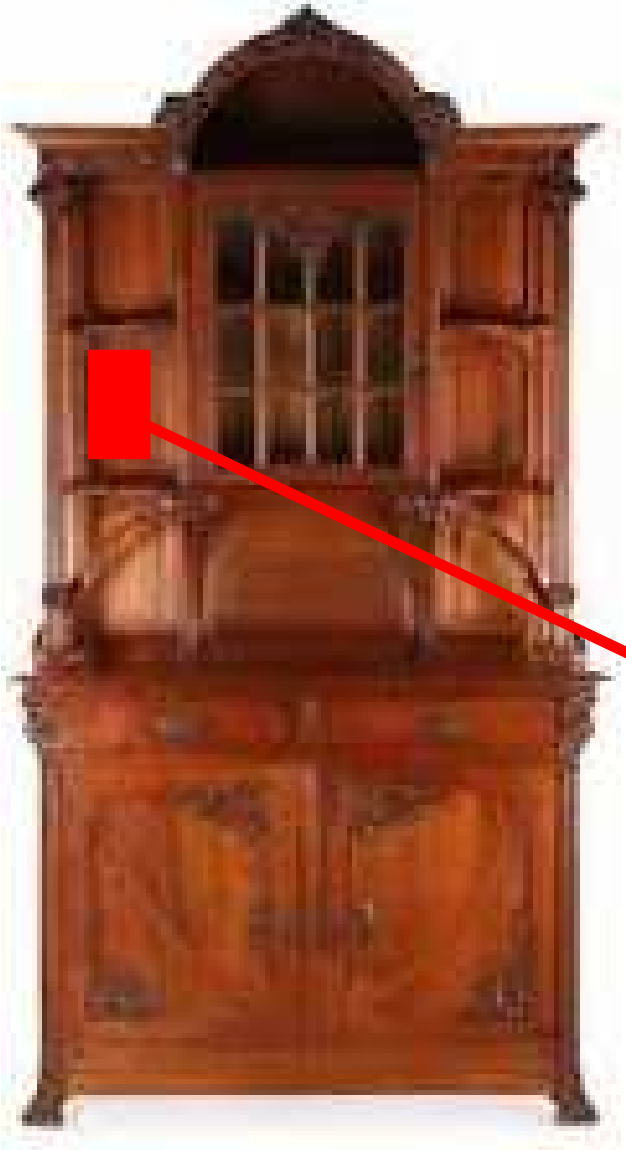


Pointer to list with one condition record

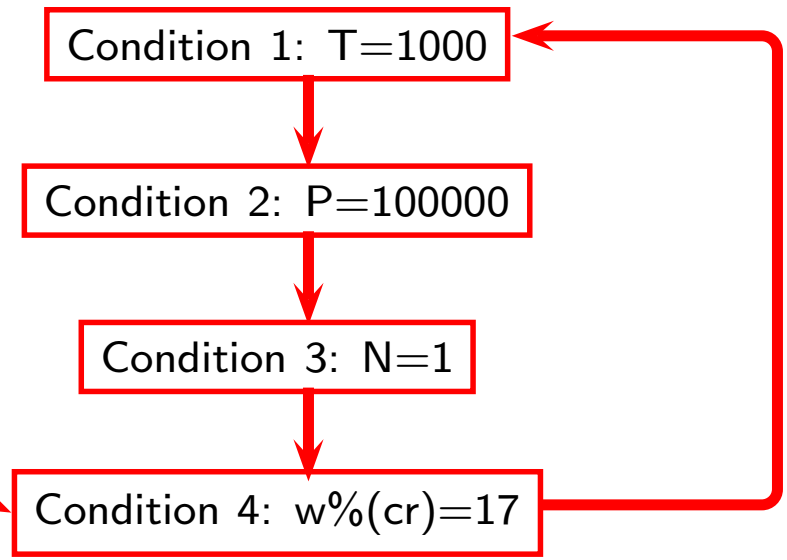


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Dynamic data: Inside the equilibrium record 2

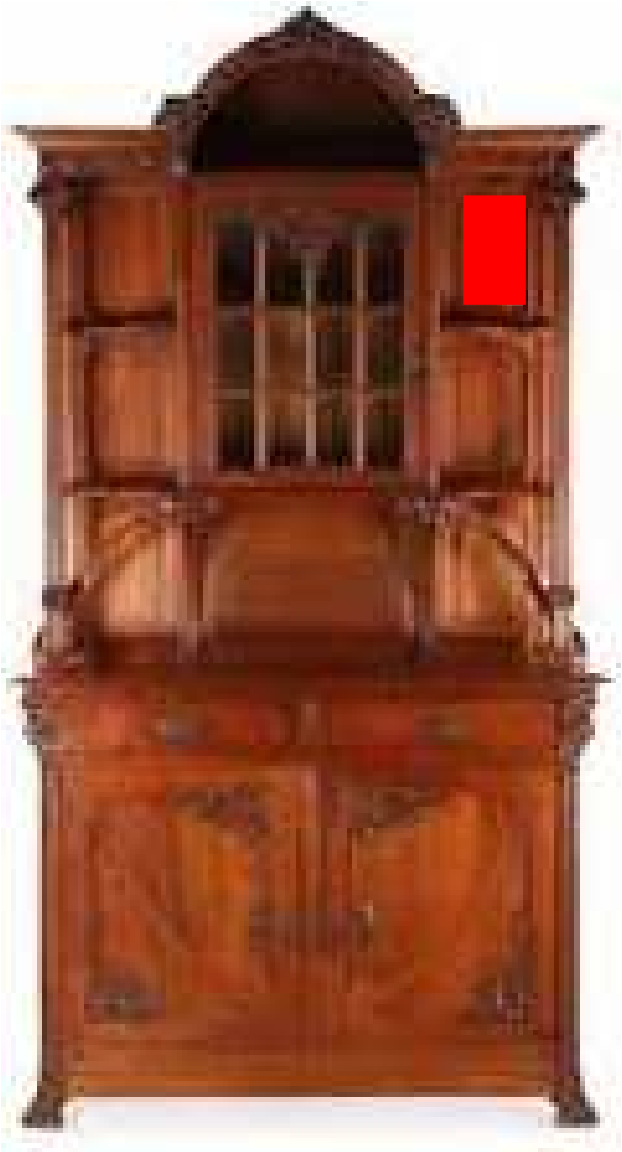


Pointer to list with more condition records



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Dynamic data: Inside the equilibrium record 2



Pointer to list with experimental data used for assessments.

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Dynamic data: Inside the equilibrium record 2



Current T and P and convergence criteria

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Dynamic data: Inside the equilibrium record 2



Values of model parameters and TP functions for the values of T and P in this equilibrium. The actual expressions for these are stored in the static data structure.

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Dynamic data: Inside the equilibrium record 2



Values of state variable functions which depend on the result of a calculation. These expressions are also stored in the static data structure.

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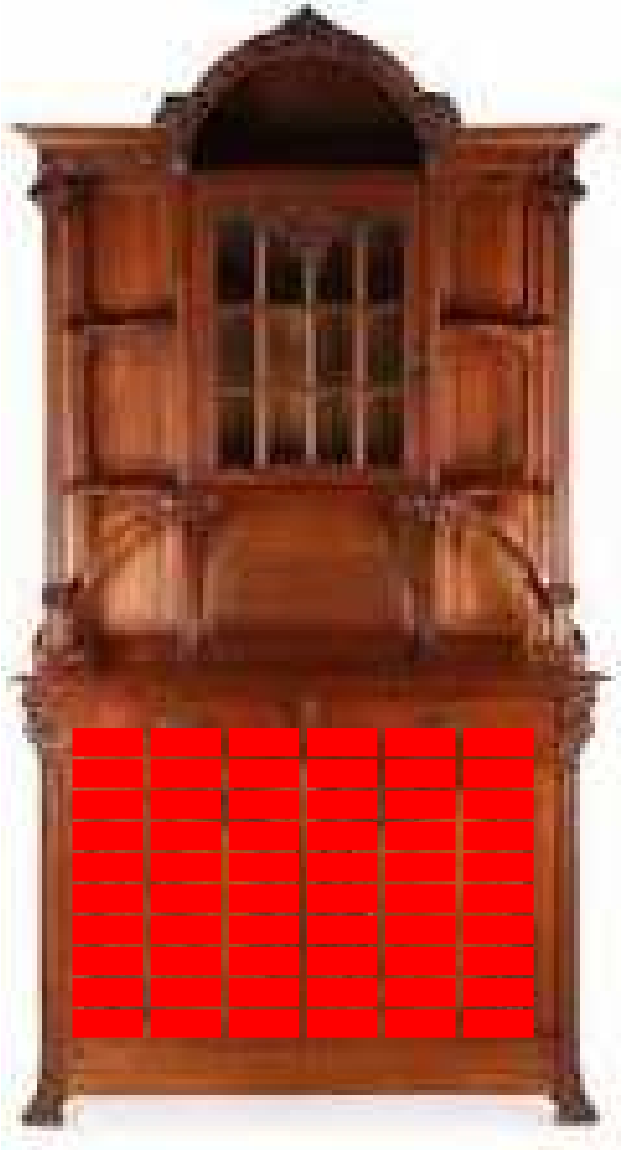
Dynamic data: Inside the equilibrium record 2



Woops ... a secret drawer (undocumented)

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Dynamic data: Inside the equilibrium record 2



The phase_varres record array:

- One entry for each phase and composition set
- Index to static phase record, phase tuple, status etc.
- Amount formula units of the phase, $\aleph^{\alpha}$
- Moles of atoms per formula unit of phase
- The number of sites on each sublattices
- A possible disordered fraction set record
- Array with constituent fractions y_{si}^{α}
- Net charge, driving force
- Number of properties, array with property type indices
- Array with G, $\frac{\partial G}{\partial T}$, $\frac{\partial G}{\partial P}$, $\frac{\partial^2 G}{\partial T^2}$ etc. and other properties
- Array with $\frac{\partial G}{\partial y_{si}}$, $\frac{\partial^2 G}{\partial y_{si}\partial T}$ and $\frac{\partial^2 G}{\partial y_{si}\partial P}$
- Array with $\frac{\partial^2 G}{\partial y_{si}\partial y_{tj}}$

Calculating the thermodynamic equilibrium

- The equilibrium algorithm
- Finding the global equilibrium
- The second derivative of Gibbs energy
- Memory leaks and other problems

Calculating the thermodynamic equilibrium

The algorithm for minimization that is implemented in OC was proposed by Hillert (1981). It uses Lagrange multipliers to minimize the total Gibbs energy with constraints:

$$G(T,P,N) = \sum_{\alpha} \aleph^{\alpha} G_M^{\alpha}(T,P,Y) \tag{10}$$

$$0 = N_{\mathrm{A}} - \sum_{\alpha} \aleph^{\alpha} M_{\mathrm{A}}^{\alpha} \tag{11}$$

$$0 = \sum_{i} y_{si}^{\alpha} - 1 \tag{12}$$

where $\aleph^{\alpha}$ is the amount of phase α, N_{A} is the total amount of component A, M_{A}^{α} is the amount of component A and y_{si}^{α} is the fraction of constituent i on sublattice s in phase α.

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$$L = \sum_{\alpha} \aleph^{\alpha} G_M^{\alpha}(T,P,Y) + \sum_{\mathrm{A}} (N_{\mathrm{A}} - \sum_{\alpha} \aleph^{\alpha} M_{\mathrm{A}}^{\alpha}) \mu_{\mathrm{A}} + \sum_{\alpha} \sum_{s} \eta_s^{\alpha} (\sum_{i} y_{si}^{\alpha} - 1) \tag{13}$$

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where μ_{A} and η_s^{α} the are multipliers for the constraints. L has the same minimum as G when the constraints are fulfilled.
At equilibrium all partial derivatives must be zero and from the derivative of the Lagrange function with respect to $\aleph^{\alpha}$ we get:

$$\frac{\partial L}{\partial \aleph^{\alpha}} = G_M^{\alpha} - \sum_{\mathrm{A}} M_{\mathrm{A}}^{\alpha} \mu_{\mathrm{A}} = 0 \tag{14}$$

The multiplier μ_{A} can thus be identified as the chemical potential of A.

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$$\sum_{\mathrm{A}} M^{\alpha}_{\mathrm{A}} \mu_{\mathrm{A}} = G^{\alpha}_{M} \tag{15}$$

The external conditions concerning extensive variables such as the amount of a component A, the T, P, the enthalpy, etc. A condition on the amount of component B, $\tilde{N}_{\mathrm{B}}$:
$N_{\mathrm{B}} = \sum_{\alpha} \aleph^{\alpha} M^{\alpha}_{\mathrm{B}} = \tilde{N}_{\mathrm{B}}$, can be formulated as a differential:

$$\Delta N_{\mathrm{B}} = \sum_{\alpha} \aleph^{\alpha} \sum_{si} \frac{\partial M^{\alpha}_{\mathrm{B}}}{\partial y^{\alpha}_{si}} \Delta y^{\alpha}_{si} + \sum_{\alpha} M^{\alpha}_{\mathrm{B}} \Delta \aleph^{\alpha} \quad = \quad N_{\mathrm{B}} - \tilde{N}_{\mathrm{B}} \tag{16}$$

where for phase α the Δy^{α}_{si} are the changes in the constituent fractions and $\Delta \aleph^{\alpha}$ is the phase amount change.

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Calculating the thermodynamic equilibrium

The equilibrium matrix is a system of equations based on the external conditions with chemical potentials and the amounts and compositions of the stable phases as variables. There is one equation for each stable phase to ensure they are on the same Gibbs energy plane:

$$\sum_{\mathrm{A}} M^{\alpha}_{\mathrm{A}} \mu_{\mathrm{A}} = G^{\alpha}_{M} \tag{15}$$

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where for phase α the Δy^{α}_{si} are the changes in the constituent fractions and $\Delta \aleph^{\alpha}$ is the phase amount change.
Eq. 16 is transformed by replacing Δy^{α}_{si} with a linear expression of the potentials, using an *inverted phase matrix*, e^{α}_{ij}, derived from the Lagrange equation (here including variable T):

$$\sum_{\alpha} \aleph^{\alpha} \sum_{si} \frac{\partial M^{\alpha}_{\mathrm{B}}}{\partial y_{si}} \left[\sum_{tj} \sum_{\mathrm{A}} \frac{\partial M^{\alpha}_{\mathrm{A}}}{\partial y_{tj}} \; e^{\alpha}_{ij} \mu_{\mathrm{A}} - \sum_{tj} \frac{\partial^2 G^{\alpha}_{M}}{\partial y_{tj} \partial T} \; e^{\alpha}_{ij} \Delta T - \sum_{tj} \frac{\partial G^{\alpha}_{M}}{\partial y_{tj}} e^{\alpha}_{ij} \right]$$
$$+ \sum_{\alpha} M^{\alpha}_{\mathrm{A}} \Delta \aleph^{\alpha} \;=\; N_{\mathrm{A}} - \tilde{N}_{\mathrm{A}}$$

where e^{α}_{ij} depends on the second derivatives of G^{α}_{M}: $\frac{\partial^2 G^{\alpha}_{M}}{\partial y_{si} \partial y_{tj}}$

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$$+ \sum_{\alpha} M^{\alpha}_{\mathrm{A}} \Delta \aleph^{\alpha} \quad = \quad N_{\mathrm{A}} - \tilde{N}_{\mathrm{A}}$$

highlighting the change.

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Calculating the thermodynamic equilibrium

The equilibrium matrix is a system of equations based on the external conditions with chemical potentials and the amounts and compositions of the stable phases as variables. There is one equation for each stable phase to ensure they are on the same Gibbs energy plane:

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$$+ \sum_{\alpha} M^{\alpha}_{\mathrm{A}} \Delta \aleph^{\alpha} \quad = \quad N_{\mathrm{A}} - \tilde{N}_{\mathrm{A}}$$

the potential variables replacing the Δy^{α}_{si}.

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Calculating the thermodynamic equilibrium

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the inverted phase matrix elements are used here.

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An example of the equilibrium matrix

For a binary A-B system (at known T, P) with two stable phases we have 4 unknown: $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$ and the change in phase amounts $\Delta\aleph^{\alpha}, \Delta\aleph^{\beta}$:

$$\begin{pmatrix} M_{\mathrm{A}}^{\alpha} & M_{\mathrm{B}}^{\alpha} & 0 & 0 \\ M_{\mathrm{A}}^{\beta} & M_{\mathrm{B}}^{\beta} & 0 & 0 \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{A}}^{\alpha} & M_{\mathrm{A}}^{\beta} \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{B}}^{\alpha} & M_{\mathrm{B}}^{\beta} \end{pmatrix} \begin{pmatrix} \mu_{\mathrm{A}} \\ \mu_{\mathrm{B}} \\ \Delta\aleph^{\alpha} \\ \Delta\aleph^{\beta} \end{pmatrix} =$$

$$\begin{pmatrix} G_M^{\alpha} \\ G_M^{\beta} \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \sum_j \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \frac{\partial G_M^{\gamma}}{\partial y_j} e_{ij}^{\gamma} + N_{\mathrm{A}} - \tilde{N}_{\mathrm{A}} \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \sum_j \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \frac{\partial G_M^{\gamma}}{\partial y_j} e_{ij}^{\gamma} + N_{\mathrm{B}} - \tilde{N}_{\mathrm{B}} \end{pmatrix}$$

An example of the equilibrium matrix

For a binary A-B system (at known T, P) with two stable phases we have 4 unknown: $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$ and the change in phase amounts $\Delta\aleph^{\alpha}, \Delta\aleph^{\beta}$:

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Even in multi-component systems with many constituent fractions we have just one μ_{A} for each component and one $\Delta\aleph^{\alpha}$ for each stable phase.
Without inverting the phase matrix this we must include constituent fractions for all stable phases and it becomes much larger and has to be solved using non-linear methods.

An example of the equilibrium matrix

For a binary A-B system (at known T, P) with two stable phases we have 4 unknown: $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$ and the change in phase amounts $\Delta\aleph^{\alpha}, \Delta\aleph^{\beta}$:

$$\begin{pmatrix} M_{\mathrm{A}}^{\alpha} & M_{\mathrm{B}}^{\alpha} & 0 & 0 \\ M_{\mathrm{A}}^{\beta} & M_{\mathrm{B}}^{\beta} & 0 & 0 \\ \sum_{\gamma} \aleph^{\gamma} \sum_{i} \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_{j} \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_{i} \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_{j} \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{A}}^{\alpha} & M_{\mathrm{A}}^{\beta} \\ \sum_{\gamma} \aleph^{\gamma} \sum_{i} \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_{j} \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_{i} \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_{j} \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{B}}^{\alpha} & M_{\mathrm{B}}^{\beta} \end{pmatrix} \begin{pmatrix} \mu_{\mathrm{A}} \\ \mu_{\mathrm{B}} \\ \Delta\aleph^{\alpha} \\ \Delta\aleph^{\beta} \end{pmatrix} =$$

$$\begin{pmatrix} G_M^{\alpha} \\ G_M^{\beta} \\ \sum_{\gamma} \aleph^{\gamma} \sum_{i} \sum_{j} \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \frac{\partial G_M^{\gamma}}{\partial y_j} e_{ij}^{\gamma} + N_{\mathrm{A}} - \tilde{N}_{\mathrm{A}} \\ \sum_{\gamma} \aleph^{\gamma} \sum_{i} \sum_{j} \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \frac{\partial G_M^{\gamma}}{\partial y_j} e_{ij}^{\gamma} + N_{\mathrm{B}} - \tilde{N}_{\mathrm{B}} \end{pmatrix}$$

After solving this linear system of equations we have new values of the chemical potentials and phase amounts and we can obtain new phase constitutions.
We can iterate until the changes in chemical potentials and fractions become less than some convergence criteria.

An example of the equilibrium matrix

For a binary A-B system (at known T, P) with two stable phases we have 4 unknown: $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$ and the change in phase amounts $\Delta\aleph^{\alpha}, \Delta\aleph^{\beta}$:

$$\begin{pmatrix} M_{\mathrm{A}}^{\alpha} & M_{\mathrm{B}}^{\alpha} & 0 & 0 \\ M_{\mathrm{A}}^{\beta} & M_{\mathrm{B}}^{\beta} & 0 & 0 \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{A}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{A}}^{\alpha} & M_{\mathrm{A}}^{\beta} \\ \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & \sum_{\gamma} \aleph^{\gamma} \sum_i \frac{\partial M_{\mathrm{B}}^{\gamma}}{\partial y_i} \sum_{\mathrm{C}} \sum_j \frac{\partial M_{\mathrm{C}}^{\gamma}}{\partial y_j} e_{ij}^{\gamma} & M_{\mathrm{B}}^{\alpha} & M_{\mathrm{B}}^{\beta} \end{pmatrix} \begin{pmatrix} \mu_{\mathrm{A}} \\ \mu_{\mathrm{B}} \\ \Delta\aleph^{\alpha} \\ \Delta\aleph^{\beta} \end{pmatrix} =$$

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If the amount of a stable phase becomes negative it means it is no longer stable and can be removed. For the metastable phases we update the constitutions and calculate the driving force and if this is positive the phase is added to the set of stable phases.
This algorithm allows a very flexible set of external conditions, such as a phase must be stable, the composition of a phase is known or an expression using two or more state variables.

An example of the equilibrium matrix

For a binary A-B system (at known T, P) with two stable phases we have 4 unknown: $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$ and the change in phase amounts $\Delta\aleph^{\alpha}, \Delta\aleph^{\beta}$:

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The only drawback is that calculating the inverted phase matrix requires that all second derivatives of the molar Gibbs energy must be implemented analytically.
But there are also advantages to have second derivatives of G

The second derivative

Implementation of a new model can be rather complicated as it requires writing code not only the equation for the molar Gibbs energy but also the first and second derivatives of the Gibbs energy.
But there are advantages having second derivatives as these makes it possible to calculate the stability matrix to check if we are inside a miscibility gap.
In the OC there is also a possibility to calculate "dot derivatives" which represent other properties that those modeled. For example:

$$H.T \quad = \quad C_P = \left(\frac{\partial H}{\partial T}\right)_{P,s_i} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N_i} = -T\left[\left(\frac{\partial^2 G_M}{\partial T^2}\right)_{P,y_{si}} + \cdots\right] \qquad (17)$$

where the $\cdots$ include all other second derivatives of G_M because even if all N_i are constant the constituent fractions y_{si} are not.
H.T is calculated as the heat capacity of a system for the current set of conditions. This calculation include contributions to the heat capacity from variation in constitution like speciation in gases or SRO in crystalline phases.

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H.T is calculated as the heat capacity of a system for the current set of conditions. This calculation include contributions to the heat capacity from variation in constitution like speciation in gases or SRO in crystalline phases.

For kinetic simulations the second derivatives of the Gibbs energy are also useful as they are needed to convert atomic mobilities to diffusion coefficients, to calculate gradients and much more.

Calculating the global equilibrium

Any iterative algorithm must have a reasonable set of starting values, i.e. a guess of the stable phases and and their constitutions.

Calculating the global equilibrium

Any iterative algorithm must have a reasonable set of starting values, i.e. a guess of the stable phases and and their constitutions.

- To ensure the calculated equilibrium is a global minimum the OC software has an initial step which calculates the Gibbs energy of all phases over a grid of compositions.
- These are treated as stoichiometric phases in a preliminary minimization to find a **set of gridpoints** representing a global minimum and fulfilling the mass balance equations. This set will have one gridpoint per component.
- This set of gridpoints for the minimum is then used as initial guess of the stable phases and their constitutions are inserted as start values for the iterative algorithm.

Calculating the global equilibrium

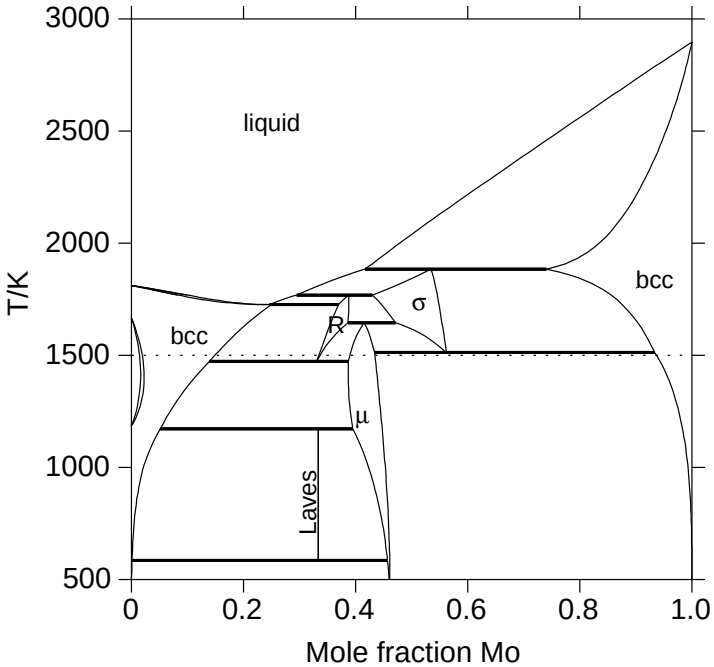
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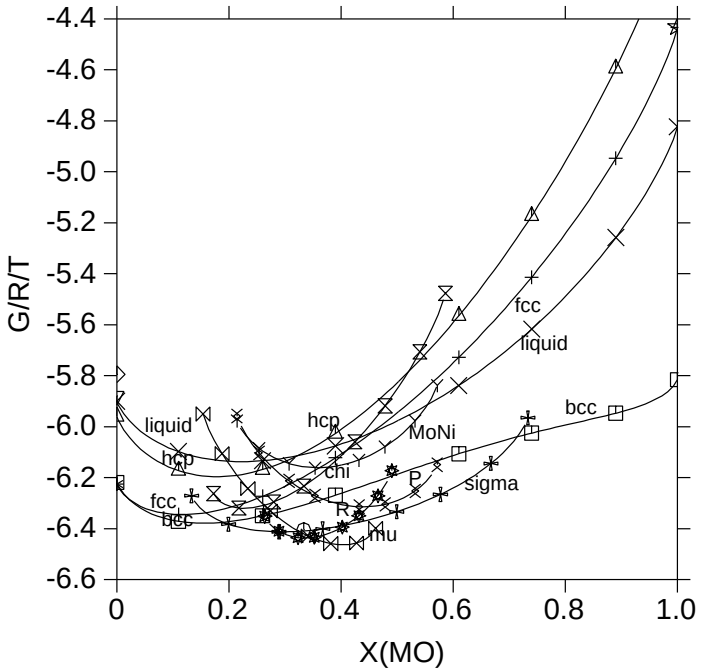
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The grid minimizer will automatically find miscibility gaps as the same phase may have several gridpoints in this set.

Grid minimizer, an example

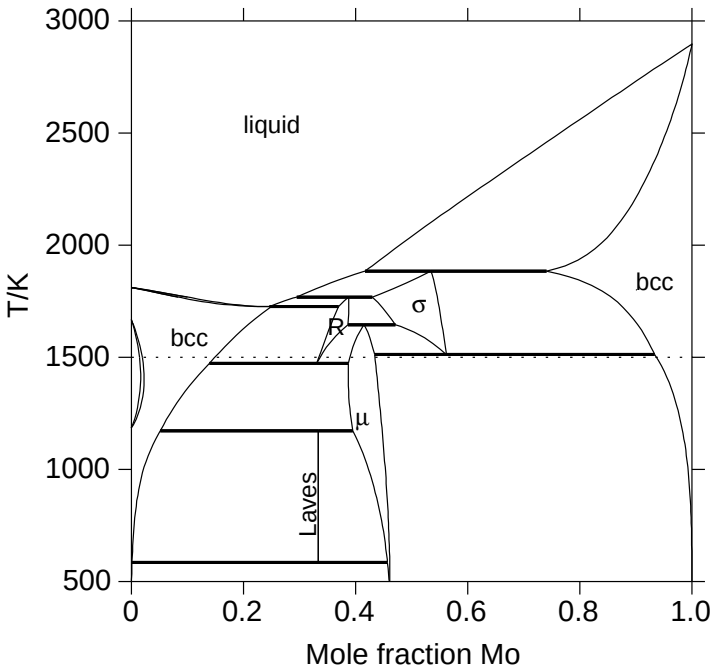
In the Fe-Mo system at 1500 K the grid minimizer calculates a number of points along the Gibbs energy curves of the different phases.

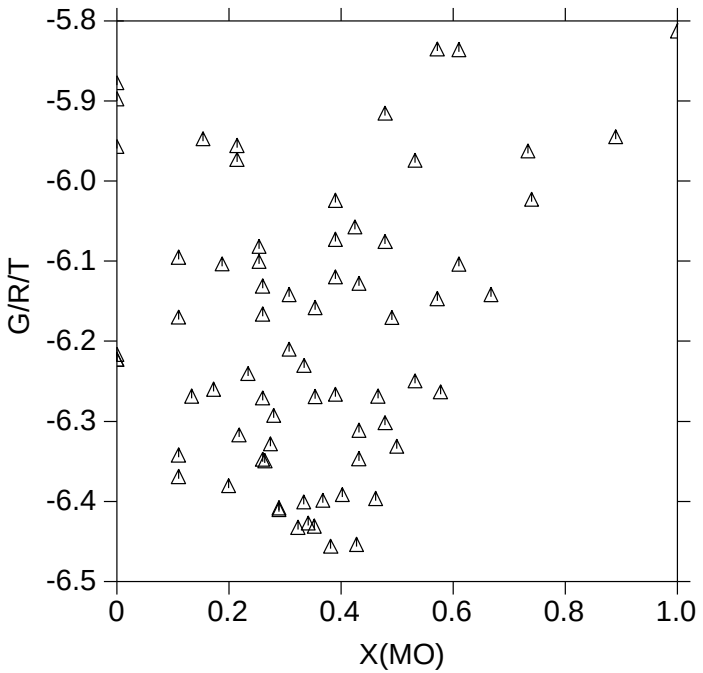




Grid minimizer, an example

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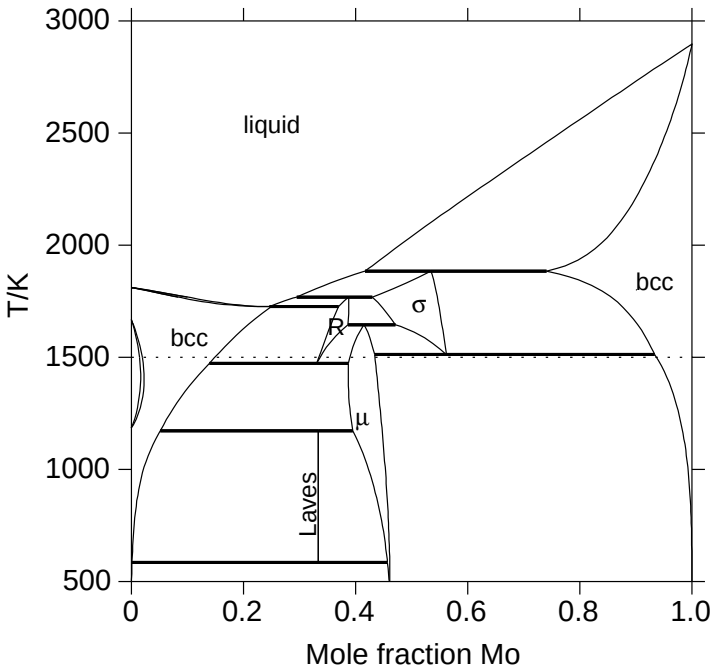


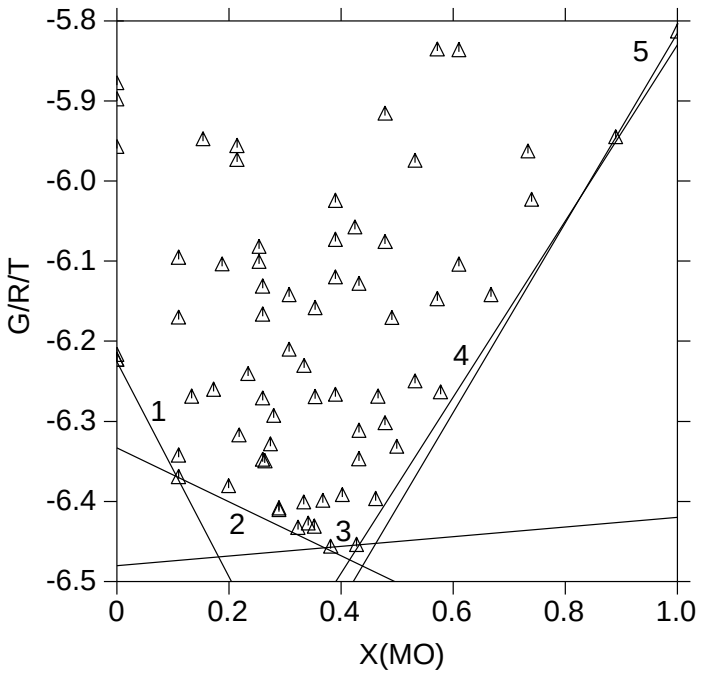


The gridpoints are treated as individual stoichiometric phases by the grid minimizer. NOTE the scale is changed!

Grid minimizer, an example

In the Fe-Mo system at 1500 K the grid minimizer calculates a number of points along the Gibbs energy curves of the different phases.

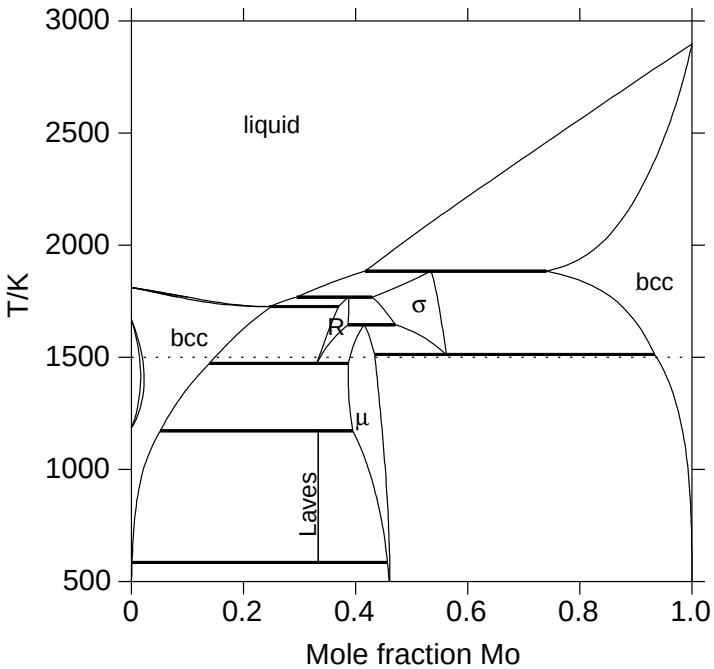


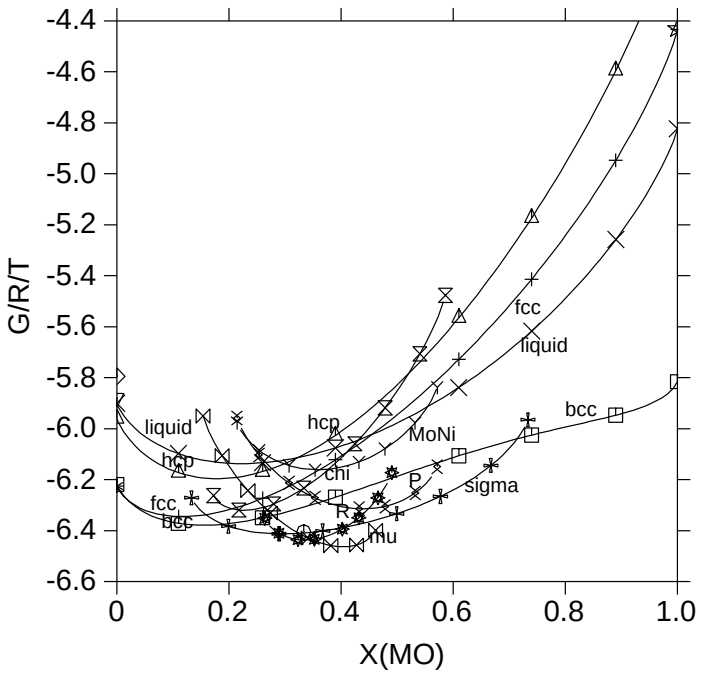


Depending on the overall composition the gridminimizer will find two points on the "convex hull" of gridpoints.

Grid minimizer, an example

In the Fe-Mo system at 1500 K the grid minimizer calculates a number of points along the Gibbs energy curves of the different phases.





These represent a composition of a solution phase and are used as start points in the iterative algorithm.

Parallelization: Memory leaks and other problems

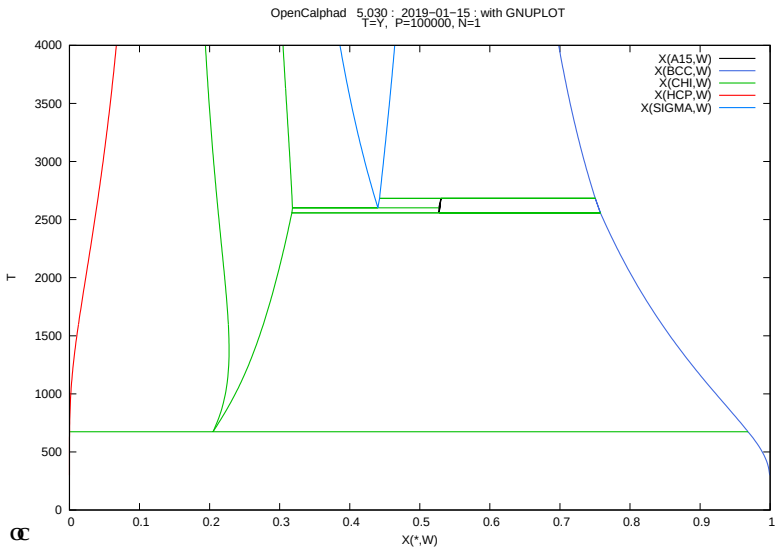
The use of records and allocatable data structures simplifies many things developing software and helps you to keep things in good order.
But it also creates new problems because if a pointer is changed by mistake you may not be able to find all your data.
There are also problems with "memory leaks" which means that memory used at the last iteration was not returned correctly to the memory pool. This means the program may crash during a large simulation due to lack of memory. The valgrind software has been a great help to eliminate this.
I had some experience using an Object Oriented language called SIMULA some 40 years ago. In SIMULA there was an automatic "garbage collector" which returned unused memory to the memory pool. But an automatic garbage collector slows down the calculations.

Phase diagrams

- Phase diagram and Gibbs energy surfaces
- Following lines
- Other ways to draw a phase diagram

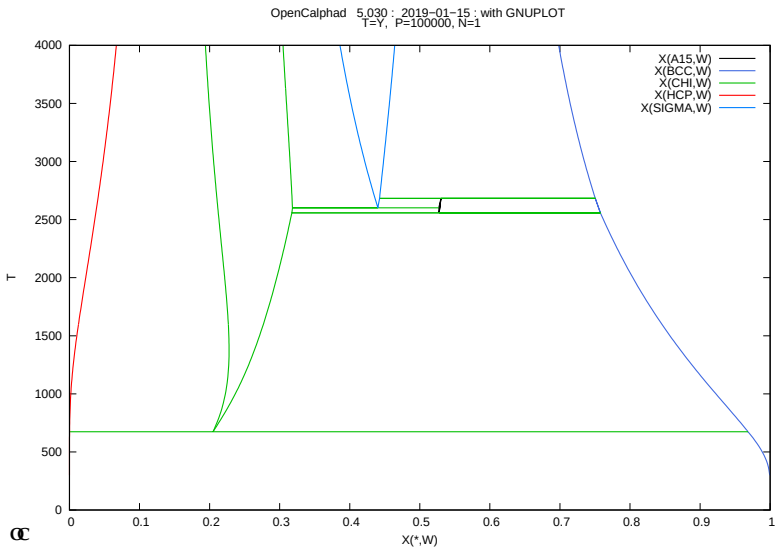
Phase diagrams and Gibbs energy curves

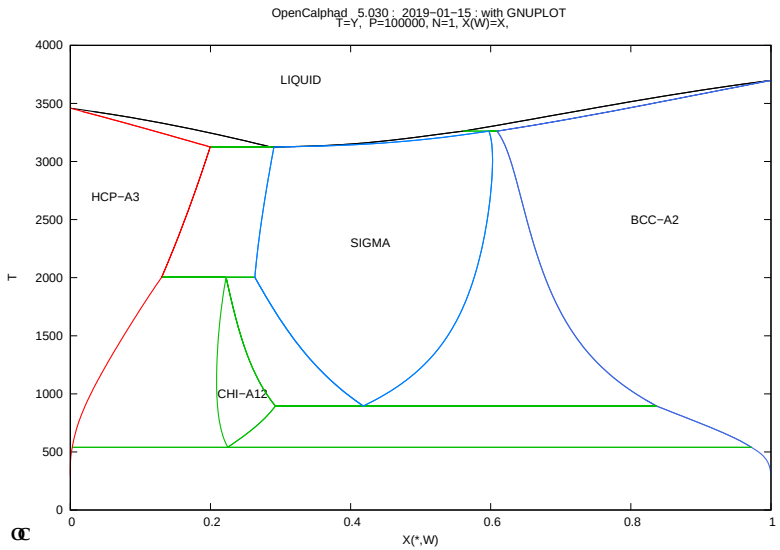
This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.



Phase diagrams and Gibbs energy curves

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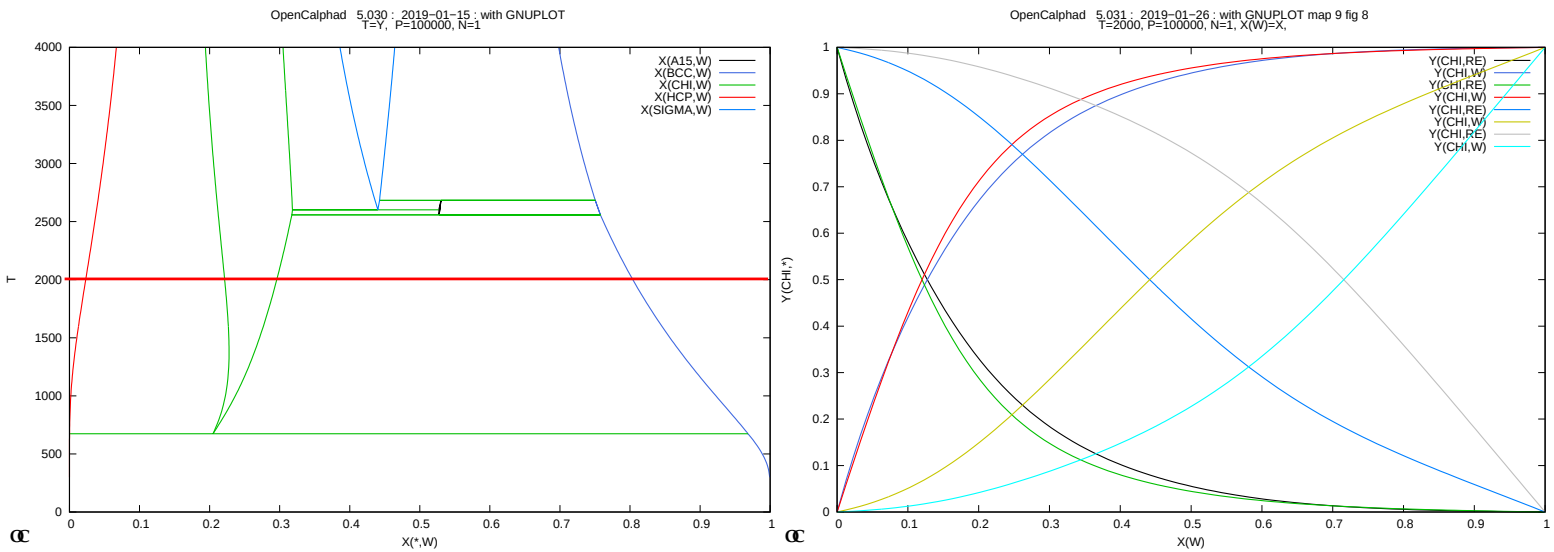




This is an assessed phase diagram using also experimental phase diagram data so using only DFT data is not always possible. But that is not my main point.

Phase diagrams and Gibbs energy curves

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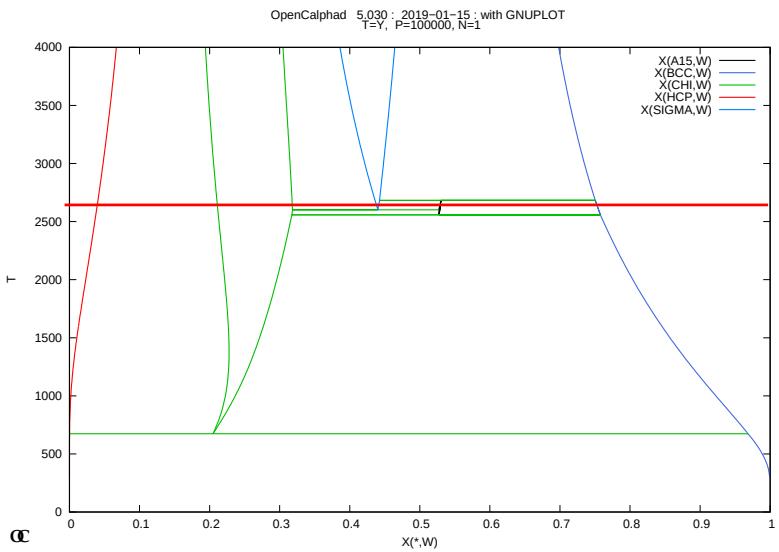


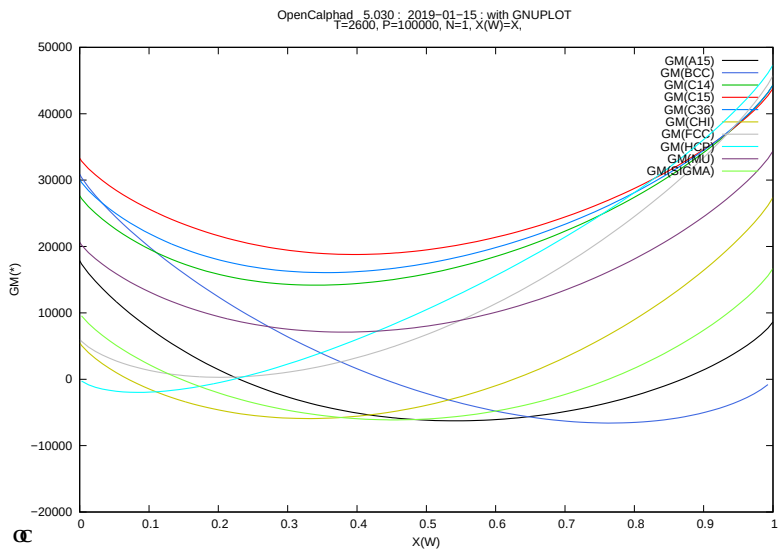
The intermetallic phases has been modeled with the crystallographically correct number of sublattices. In the diagram to the right the fraction of different constituents on the 4 different sublattices in the CHI phase at 2000 K are plotted as functions of the composition. The CHI phase is stable ony in a small composition range.
$(Re,W)_1(Re,W)_4(Re,W)_{12}(Re,W)_{12}$

But this is not my main point either.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.





The diagram to the right shows the Gibbs energy curves for all phases at 2600 K using HCP as reference state for Re and BCC for W. There is one curve for each TCP phase included in the DFT calculations: A15, C14, C15, C36, ξ, μ, σ.

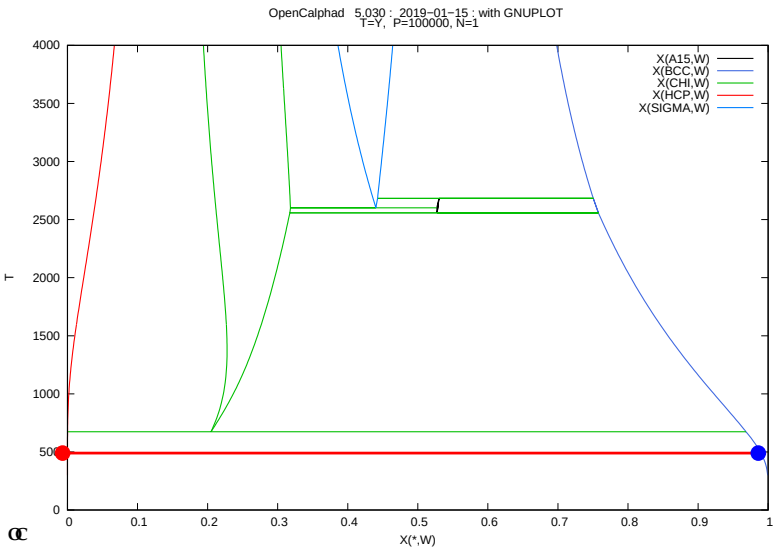
The phase diagram has only the stable set of phases given by the lowest Gibbs energy, the "convex hull".

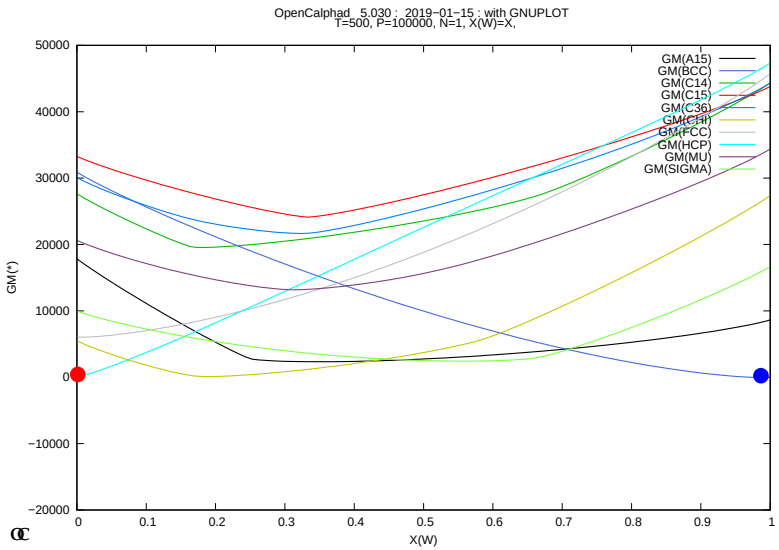
Many of the Gibbs energy curves are very close and small uncertainties in the values of the DFT calculations are significant for the stability.

The metastable ranges of the Gibbs energy curves are also important because changing T or adding a third element will change these curves. We need to know how a metastable phase behaves in the binary.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.



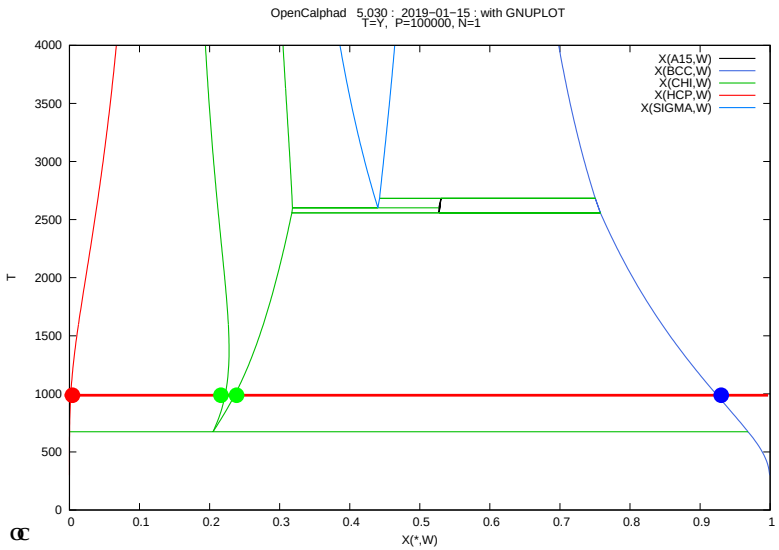


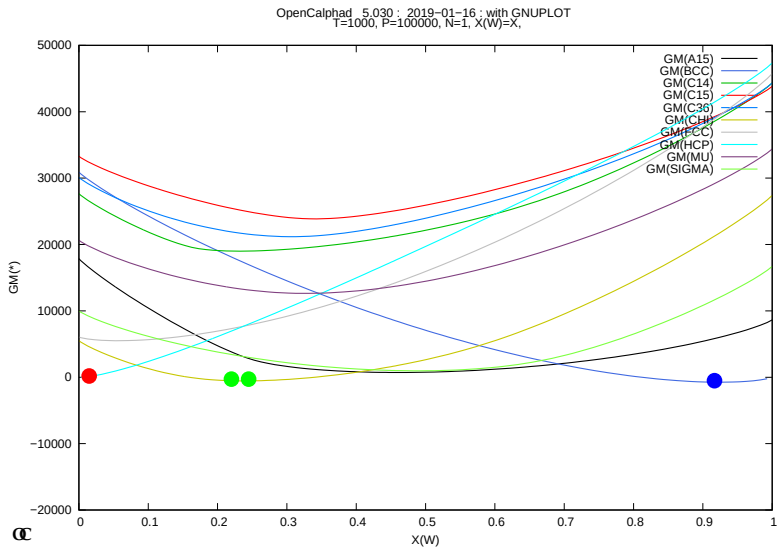
Here are the curves at 500 K. The points in both diagrams indicate the solubility limits of the stable phases in the phase diagram. At this T we have just the HCP and BCC phases stable with small solubilities.

The Gibbs energy is zero because the reference states for the pure elements are HCP for Re and BCC for W at the current T.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.

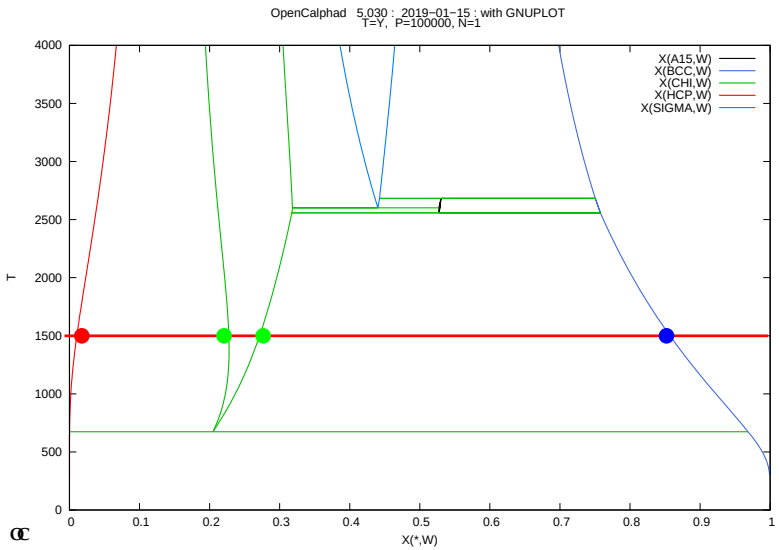


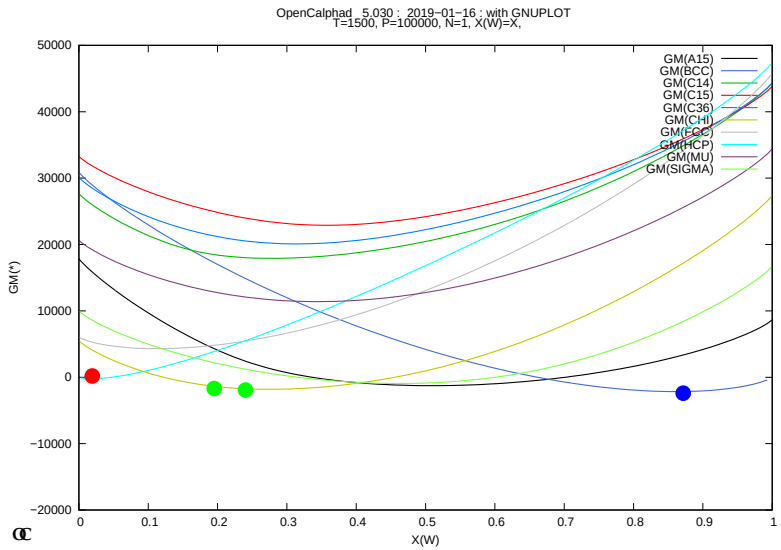


Here are the curves at 1000 K, now the CHI phase (χ), is stable.
The two green dots on the Gibbs energy curves for the CHI phase corresponds to the two dots on the solubility curves in the phase diagram, representing the compositions with a common tangent with the HCP and BCC phases respectively.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.

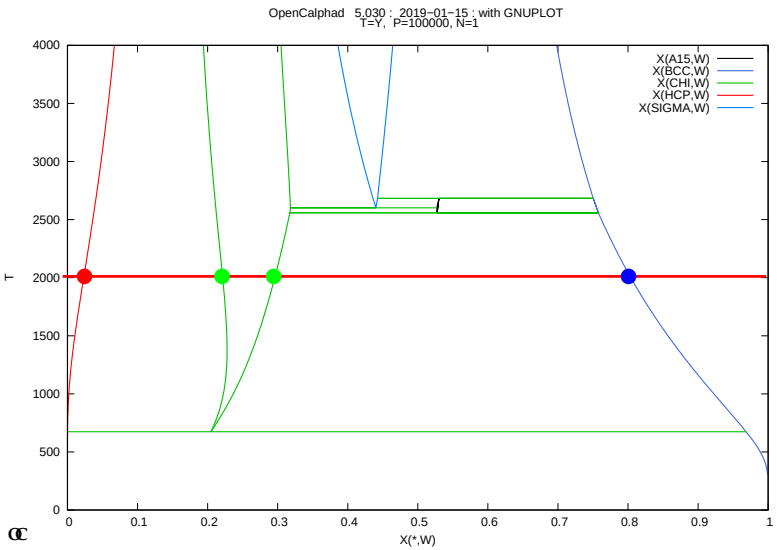


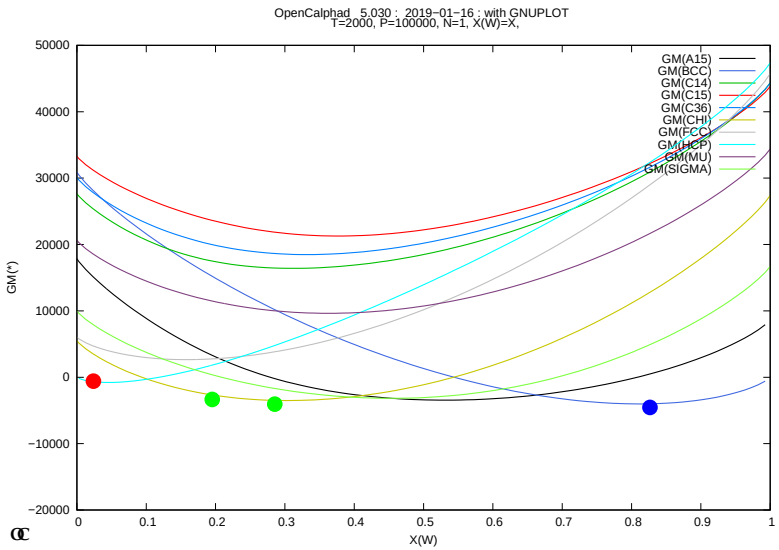


Here are the curves at 1500 K, the solubility range of the CHI phase is larger and also the solubility of Re in BCC.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.

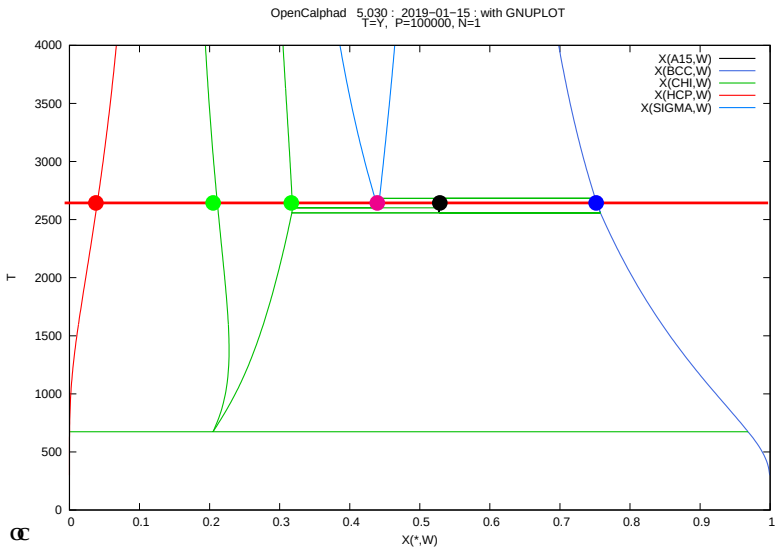


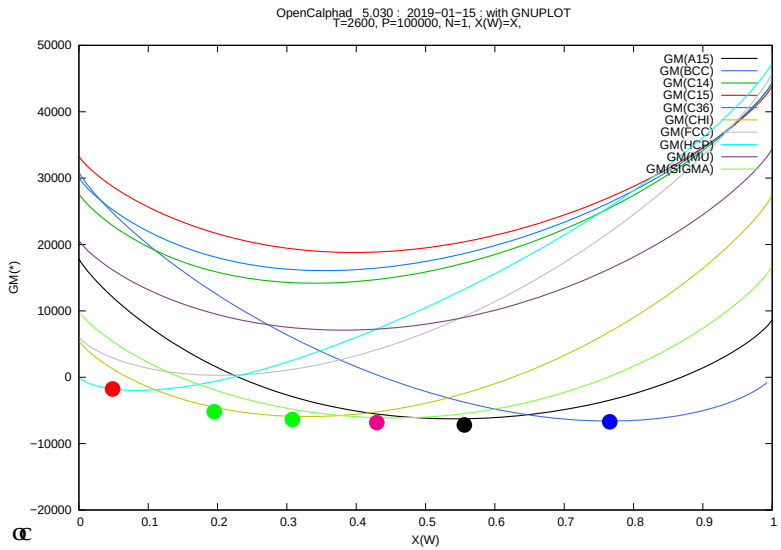


Here are the curves at 2000 K.

Phase diagrams and Gibbs energy curves

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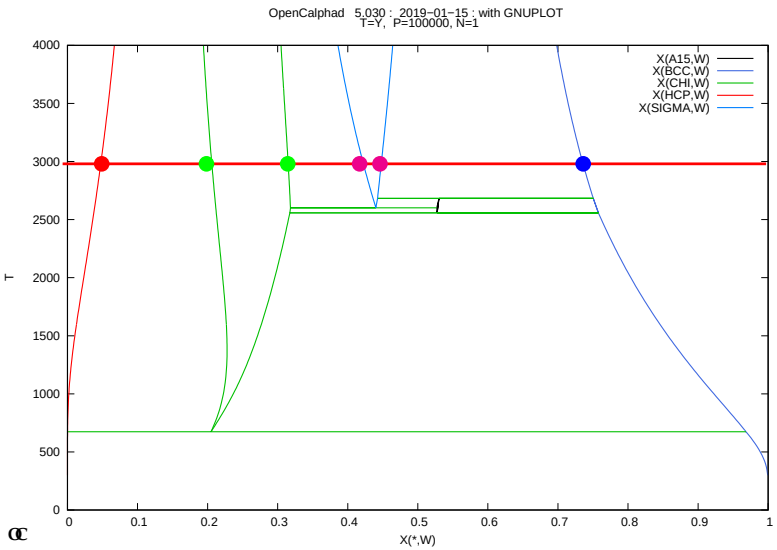


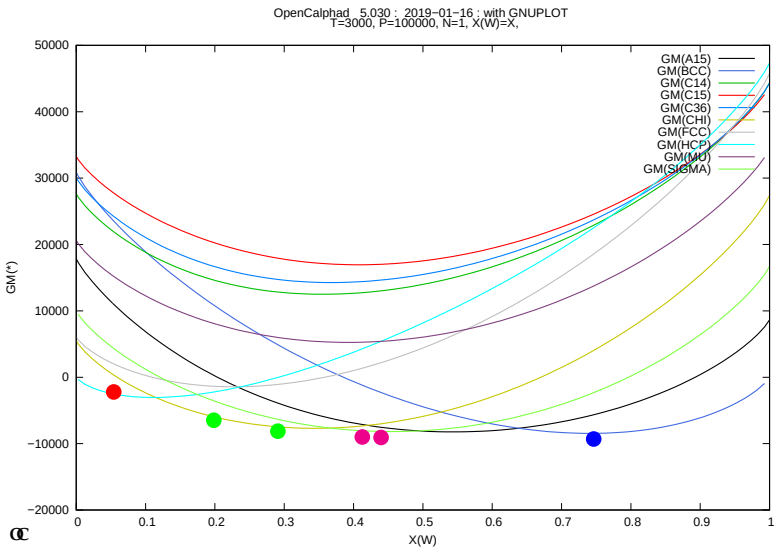


Here are the curves at 2600 K again. The SIGMA (σ) and A15 phases are also stable at this T.

Phase diagrams and Gibbs energy curves

This is a binary phase diagram for Re-W calculated using CEF with endmember energies generated by DFT.



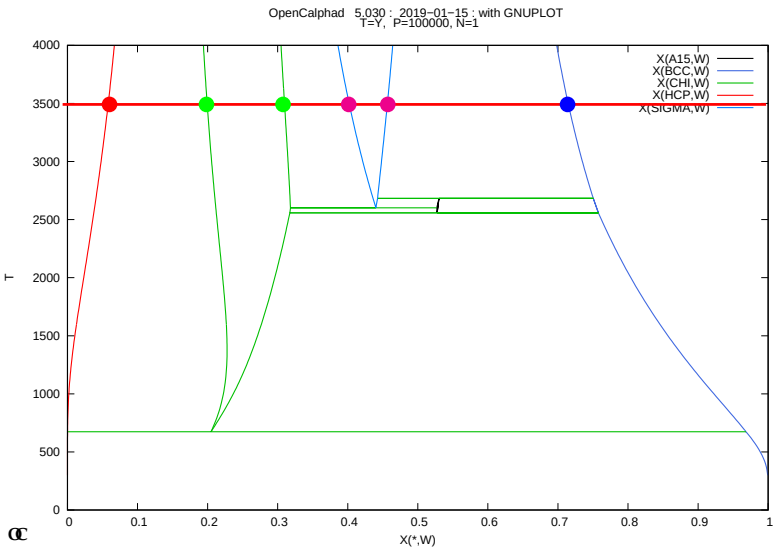


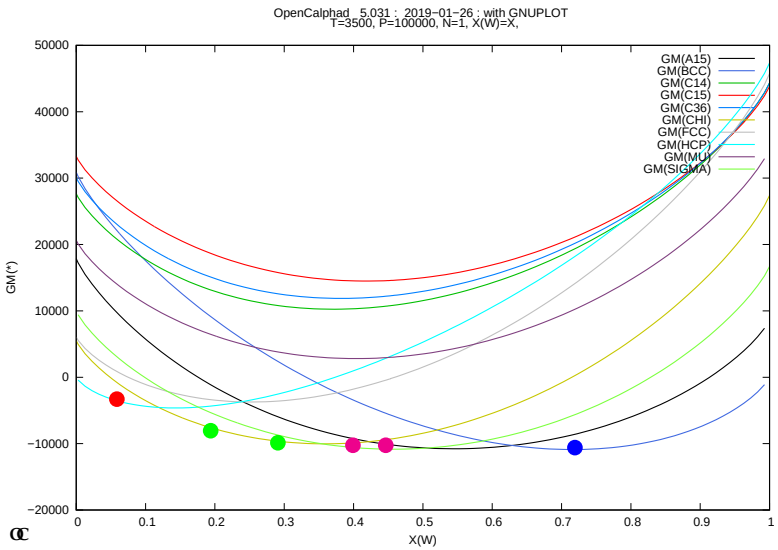
Here are the curves at 3000 K. HCP, CHI, SIGMA and BCC are stable. A15 is no longer stable but one can see it is very close to be stable from the Gibbs energy curves in the diagram to the right.

There is no liquid because there are no DFT data for the liquid phase.

Phase diagrams and Gibbs energy curves

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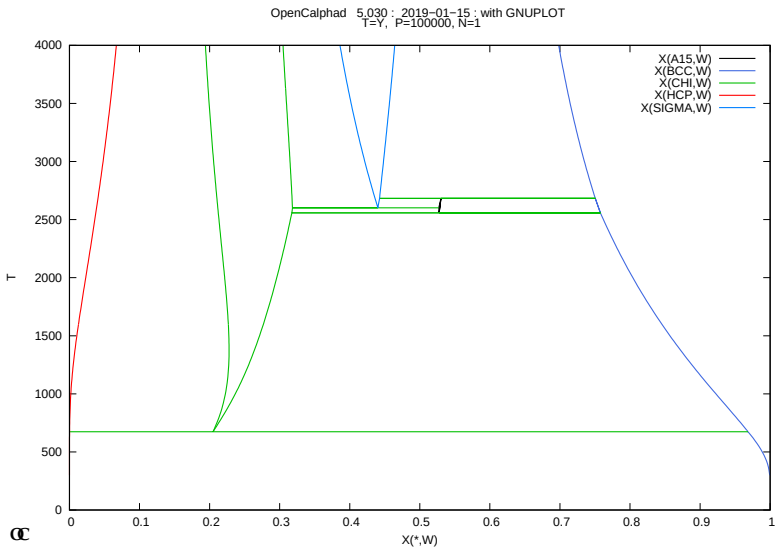


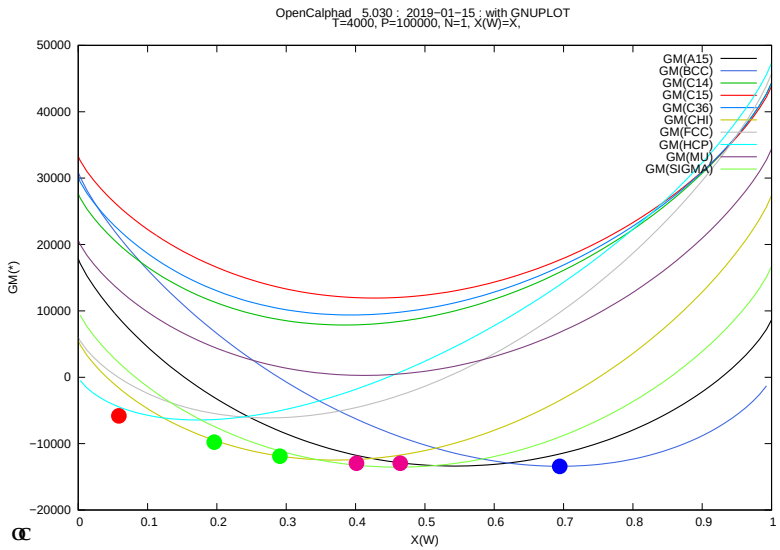


Here are the curves at 3500 K, no change of the stable set of phases.

Phase diagrams and Gibbs energy curves

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Finally the curves at 4000 K.

My intention is to show that there are a lot of Gibbs energy curves (and subsequent model parameters) behind even a few solubility lines in the stable phase diagram. It is not trivial to adjust the large number of model parameters for these phases to change the set of stable phases at varying T to obtain the correct phase diagram.
We cannot ignore the Gibbs energy curves for the metastable phases in binary systems, adding a small amount of a third element may make it stable ...

Phase diagram mapping

Using Gibbs energy curves to explain the calculation of phase diagrams can be instructive but when calculating a phase diagram there is no need to calculate the whole Gibbs energy surface for each phase to find the points of tangency shown in the phase diagram.

Phase diagram mapping

The lines in a phase diagram specifies where a phase is on its limit of stability and the equilibrium algorithm allows a condition that a phase must be fix with zero amount.
The algorithm to calculate a phase diagram is to follow a stability line of a particular phase until we reach the axis limits or a node point when the set of stable phases change.

Phase diagram mapping

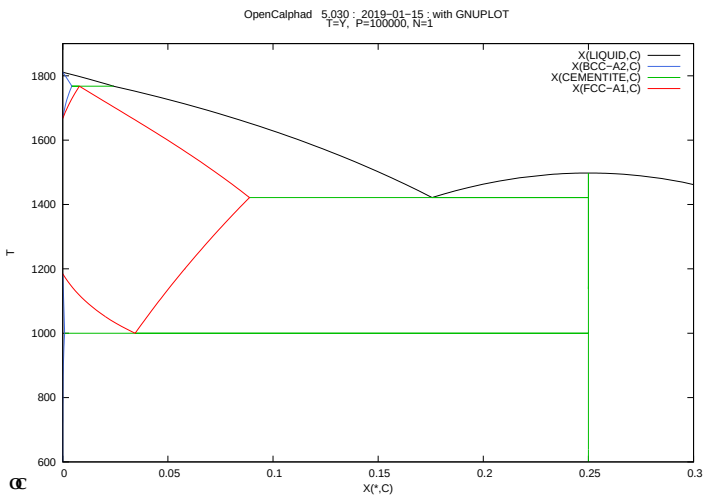
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At the node an equilibrium with two fix phases is calculated and new lines exiting from the node are generated. The number of lines exiting from a node point can vary in particular if the node point represent an invariant equilibrium.

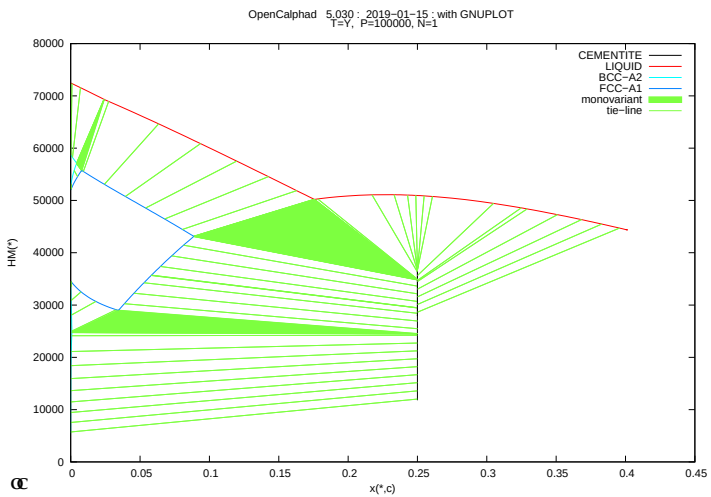
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This algorithm works for binary, ternary and multi-component systems with arbitrary number of stable phases. Unless all conditions (except one) are potentials, or a stable phase has fixed composition, the number of stable phases changes by one when crossing a line in the diagram (again with one exception: not if the line represent an invariant).

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In OC all results for each equilibria calculated during the mapping are saved and for the plotting any calculated property can be selected on the plot axis. In this way we can plot either the T or $HM(*)$ vs carbon content for the metastable Fe-C system.





Kinetic data and simulations

- Application software interface and iso-C interface
- OpenCalphad Application Software Interface, OCASI
- Mobilities, diffusivities and Darken stability matrix
- Example of a simulation

OCASI software interface

The OC software interface follows the TQ standard proposed in 1994 and which is used by Thermo-Calc and ChemApp (in slightly different forms). The OC variant is called OCASI.

- The OC software can be used by applications written in Fortran, C++, Python etc using the iso-C standard.

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- A number of applications programs are provided with the source code.

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To simulate phase transformations we need also other data than thermodynamic, for example mobilities, surface energies and thermal conductivity.

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Within OC it is possible to include these data in the same way as thermodynamic data. For example the mobility of a Al in the FCC phase has a symbol **MQ&AL(FCC)** and can be modeled as a function of T, P and composition in the same way as the Gibbs energy.

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To convert mobilities to diffusion coefficients we need the Darken stability matrix which is the determinant of all derivatives of the partial Gibbs energies (chemical potentials) with respect to the components. For a binary system the determinant of the stability matrix is simply:

$$\det(M) = \frac{\partial G_{\mathrm{A}}^{\alpha}}{\partial x_{\mathrm{A}}} \frac{\partial G_{\mathrm{B}}^{\alpha}}{\partial x_{\mathrm{B}}} - \frac{\partial G_{\mathrm{A}}^{\alpha}}{\partial x_{\mathrm{B}}} \frac{\partial G_{\mathrm{B}}^{\alpha}}{\partial x_{\mathrm{A}}} \tag{18}$$

Multi-component Darken stability matrix and 2nd derivatives

In a multi-component system the partial derivatives are slightly more complicated

$$\frac{\partial G^{\alpha}_{\mathrm{A}}}{\partial x_{\mathrm{B}}} = \frac{1}{N}\left[\left(\frac{\partial^2 G^{\alpha}_{M}}{\partial x_{\mathrm{A}}\partial x_{\mathrm{B}}}\right)_{T,P,x_{\mathrm{C}\neq\mathrm{A},\mathrm{B}}} - \sum_{\mathrm{C}} x_{\mathrm{C}}\left(\left(\frac{\partial^2 G^{\alpha}_{M}}{\partial x_{\mathrm{A}}\partial x_{\mathrm{C}}}\right)_{T,P,x_{\mathrm{D}\neq\mathrm{A},\mathrm{C}}} + \left(\frac{\partial^2 G^{\alpha}_{M}}{\partial x_{\mathrm{B}}\partial x_{\mathrm{C}}}\right)_{T,P,x_{\mathrm{D}\neq\mathrm{B},\mathrm{C}}}\right) + \sum_{\mathrm{C}}\sum_{\mathrm{D}} x_{\mathrm{C}}x_{\mathrm{D}}\left(\frac{\partial^2 G^{\alpha}_{M}}{\partial x_{\mathrm{C}}\partial x_{\mathrm{D}}}\right)_{T,P,x_{\mathrm{E}\neq\mathrm{C},\mathrm{D}}}\right] \tag{19}$$

where the summation over C and D are for all components.

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where the summation over C and D are for all components.
It is quite interesting that this is symmetric:

$$\frac{\partial G_{\mathrm{A}}^{\alpha}}{\partial x_{\mathrm{B}}} = \frac{\partial G_{\mathrm{B}}^{\alpha}}{\partial x_{\mathrm{A}}} \tag{20}$$

In the OC software all second derivatives of the Gibbs energy are calculated analytically which makes it very fast to obtain this.

OCASI example

An aluminium company in France has converted a software they used for simulating solidification and homogenization to use OCASI.

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For this alloy

Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr	Al
0.06	0.06	1.8	0.1	2.3	8.1	0.06	0.06	rest

using a simulation model including back diffusion and with their own software it took about 3.5 days to simulate the solidification and several subsequent homogenization steps.

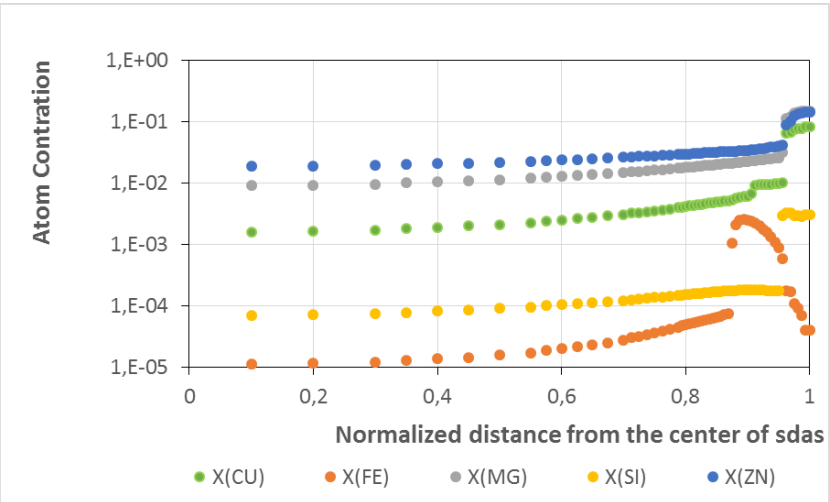
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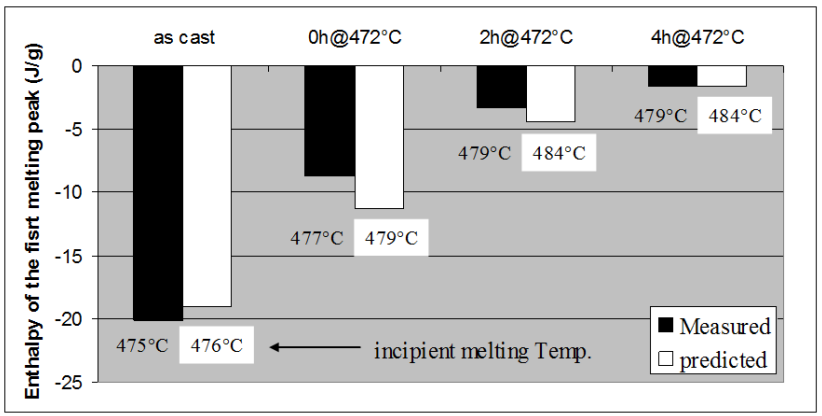
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The left hand figure show the concentration profiles across a dendrite after solidification, the right the heat evolved during homogenization.

Implementing OCASI for this simulation and running sequentially it required about 2 days. Running it in parallel with 12 CPU (24 treads) the simulation time was less than 4 hours, a reduction by 12.

Assessments - database development

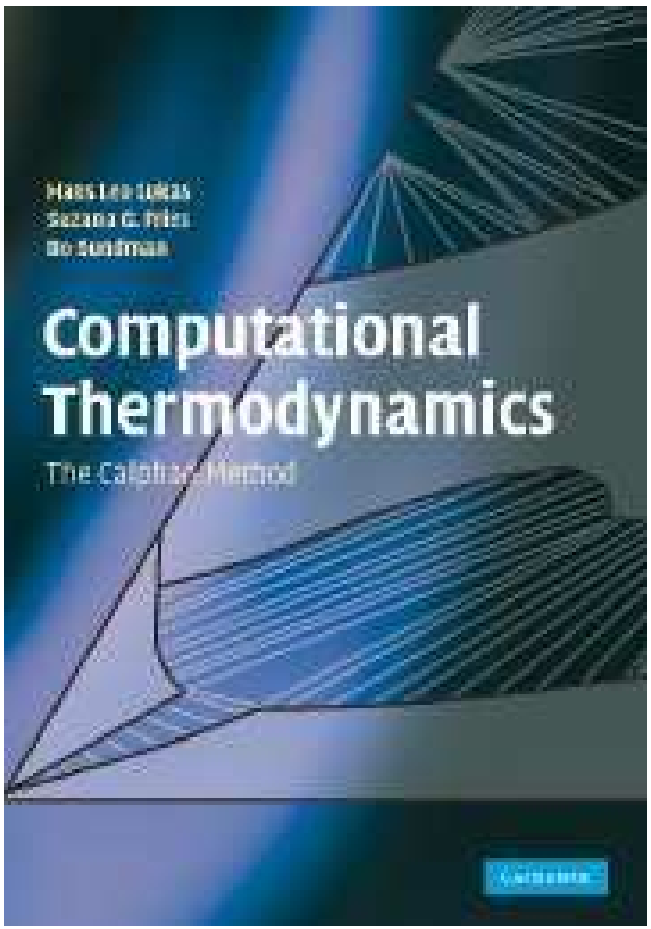
- Assessment of binary and ternary systems
- Extrapolation from Cr-Mo to a six component duplex stainless steel
- From assessments to databases

Assessing a binary or ternary system

Published assessments are the base of thermodynamic databases and are normally performed by a master or PhD student, hopefully guided by an experienced postdoc or professor. It is very challenging to select models for the phases and to understand how the parameters in the models can be adjusted to the available data.

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There is no regular training in this, and just one textbook



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In France we have arranged summer schools a few times to explain how to include all the different types of data: phase diagram, enthalpy of mixing and formation, activities and chemical potentials, heat capacities, DFT data etc. We are grateful that Mark has been teaching about DFT calculations at some of these occasions.



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A recent trend is to make assessment using mainly endmember data calculated by DFT but the uncertainties in such calculations is too large to ignore other data, in particular from phase diagrams.
It is important to use correct crystallographic models and not the earlier simplified models with reduced number of sublattices used in many of the current commercial databases.

Assessing a binary or ternary system

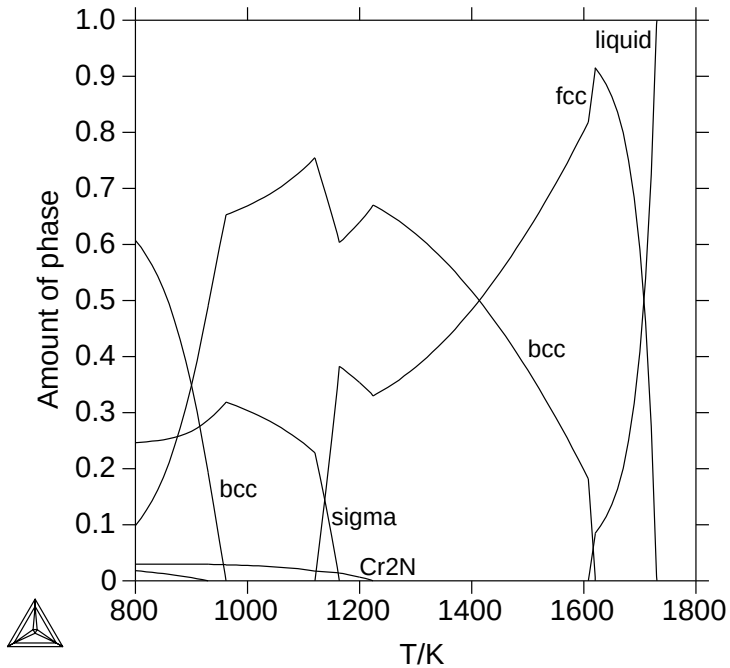
Published assessments are the base of thermodynamic databases and are normally performed by a master or PhD student, hopefully guided by an experienced postdoc or professor. It is very challenging to select models for the phases and to understand how the parameters in the models can be adjusted to the available data.

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It is important to use correct crystallographic models and not the earlier simplified models with reduced number of sublattices used in many of the current commercial databases.

Developing databases is difficult, I have an example how a problem reproducing a well established experimental information in a multi-component system could be traced back to a bad estimate of a model parameter in a binary system.

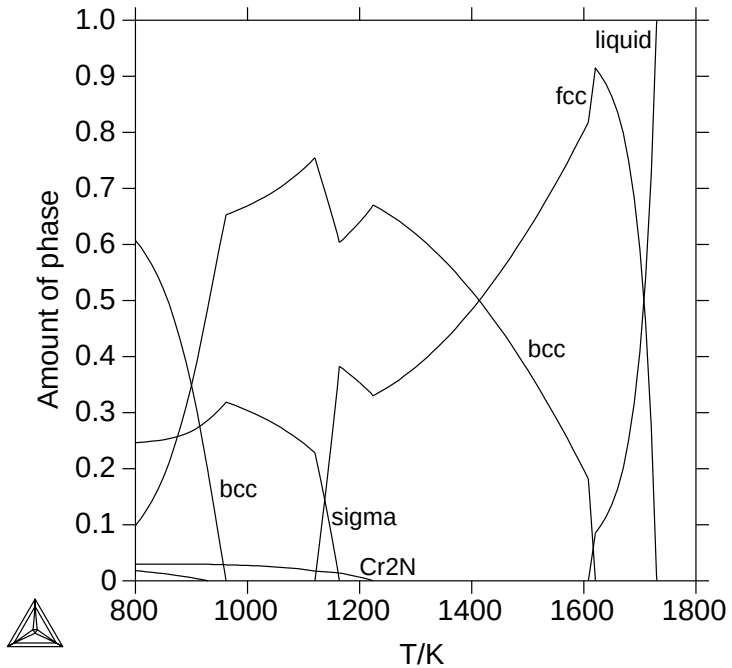
Extrapolation from a binary to SAF2507

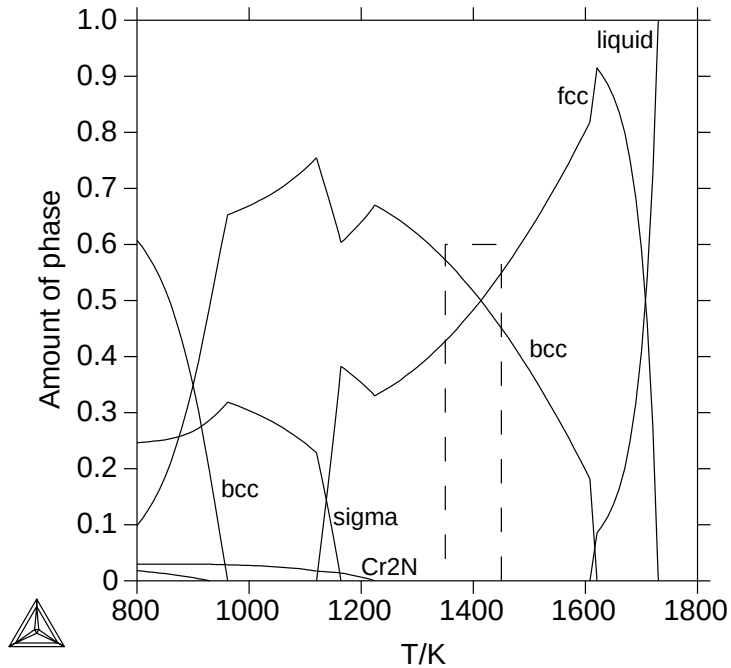
Developing a steel database we tried to calculate equilibria in the SAF 2507 duplex stainless steel with Fe-Cr-Ni-Mo-N. But we found that the FCC phase was too stable and we could not correct this using ternary or higher order parameters.



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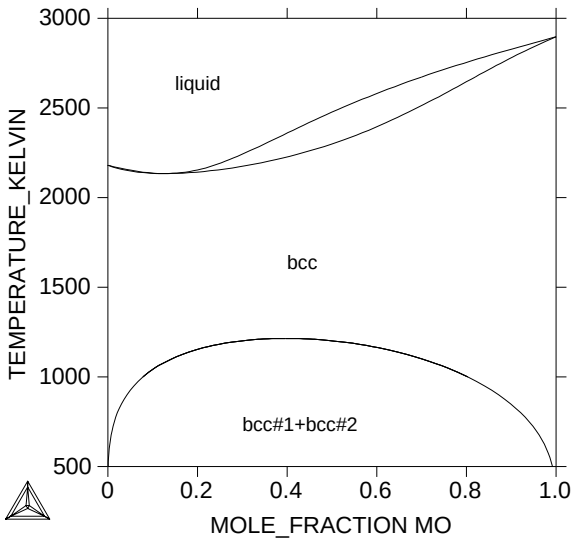


The dashed square represent the temperature "window" for heat treatment to obtain the duplex structure.

Varying all kinds of ternary or quaternary parameters did not work without creating significant changes to the fit to other data.

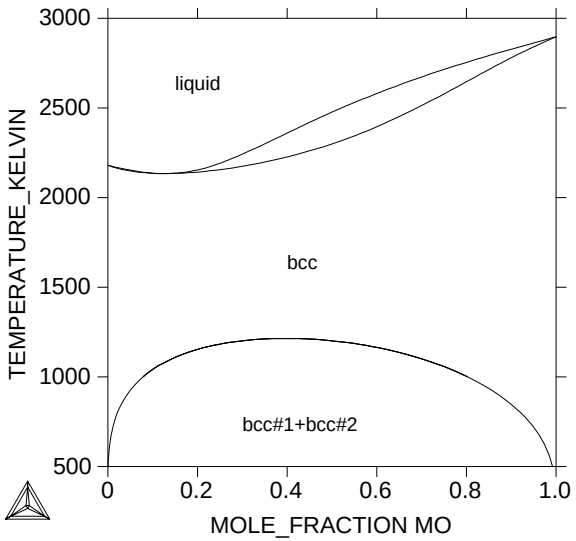
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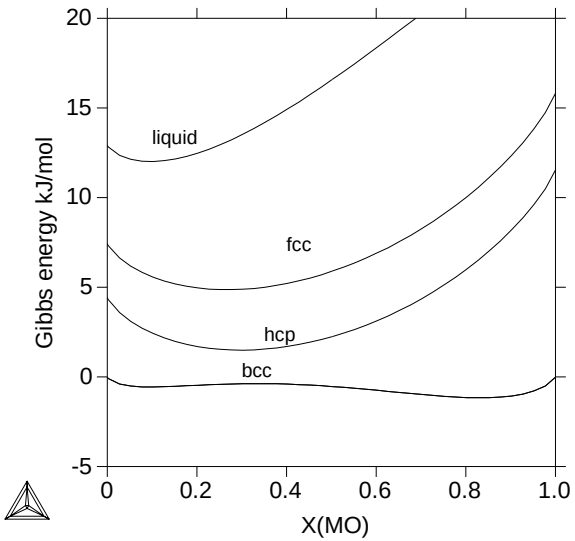
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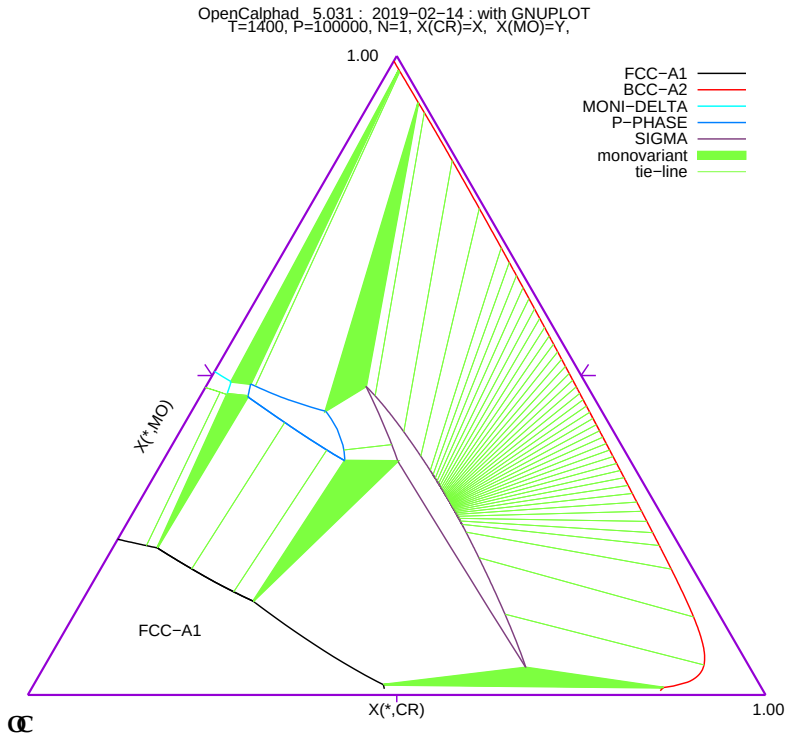




In the right had figure the Gibbs energy curves for BCC, HCP, FCC and liquid at 1000 K are plotted. There is a miscibility gap in the BCC but FCC and HCP have ideal mixing because they are not stable in the binary system.

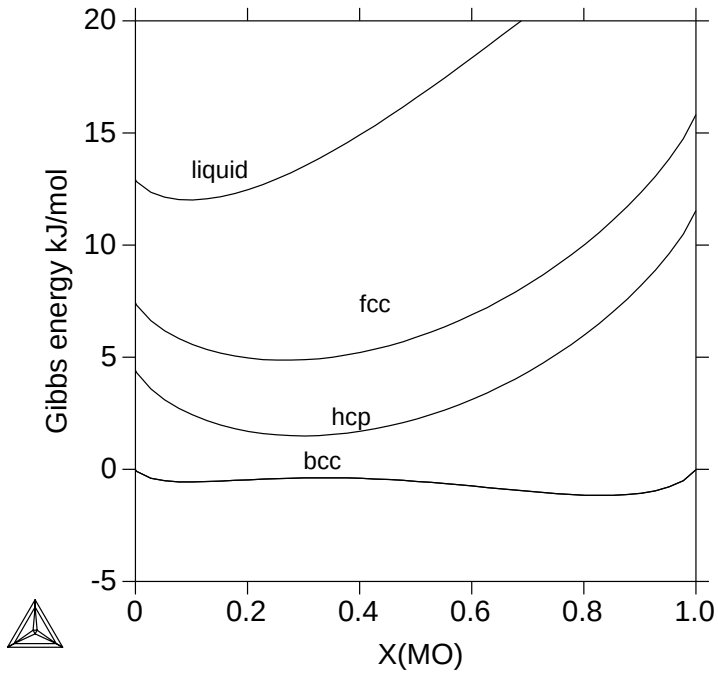
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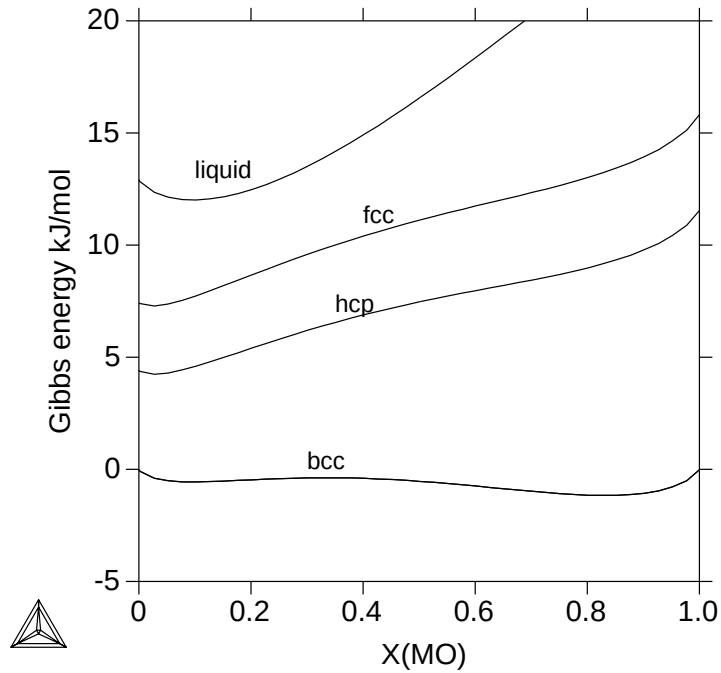
The ideal mixing in FCC does not cause any problem in the binary and in the ternary Cr-Mo-Ni where the FCC phase is stable with considerable solubility of Cr and Mo. The ternary solubility can be fitted with a small ternary interaction parameter but in higher higher order systems with low Ni content the ideal binary FCC in Cr-Mo extrapolates badly.



Extrapolation from a binary to SAF2507

Introducing a positive binary interaction in FCC Cr-Mo, similar to that in BCC can be balanced by a more negative ternary interaction in Cr-Fe-Ni to fit the large ternary solubility. And the positive binary interaction in the FCC binary Cr-Mo gives better results in the Cr-Fe-Mo-N-Ni system.





Conclusion: parameters for simple structures like BCC, FCC, HCP, should always be assessed or estimated in binary systems even if they are not stable.
Those phases which are not stable in the system should have parameters similar to the stable phase.

Including data from DFT and MD

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Stating this there are certainly many ways the software available for assessments can be improved and provide help to inexperienced users and students. Unfortunately this is a low priority topic for most commercial companies providing thermodynamic software.

Modeling the liquid is still a big challenge. In my opinion there is no good general model for the liquid and I am still searching for a model which can describe water, molten salts and metallic liquids with a single Gibbs energy expression.

From assessments to databases

Development of thermodynamic databases is a major activity of the commercial vendors of thermodynamic software.
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The manager of a multi-component database must ofen adjust the published assessments as the models are not always compatible with those used in the database. He or she must also estimate endmember values and sometimes excess parameters for phases that are not present in the database when a new component is added which can dissolve in an existing phase. This require thorough testing as well as experience and skill.

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Commercial vendors of thermodynamic software have invested a lot of money and efforts in the databases they market but for that reason they are not always interested to develop new models, unless they are small modifications of the models they already use.

From assessments to databases

When extrapolations work we have a happy database manager



From assessments to databases

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But frequently there are problems merging assessments making the database manager worried.

Summary

OpenCalphad is a free software and can be downloaded, modified, compiled and run on any computer that has a compiler for the Fortran 2008 standard. It has a modular structure for models, calculations, mapping, graphics and assessments.

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The development of new thermodynamic models is very important and there is a risk that the commercial companies loose interest in developing new models as they have invested considerable efforts and money in their current databases which will be very costly to modify.

Current status

What is working:

- CEF and ionic liquid model
- Reading (unencrypted) TDB files and entering data interactively
- Command oriented user interface with macro facilities
- Setting many different types of conditions
- Calculating multi-component equilibria
- STEP calculation of property diagram
- MAP of multi-component phase diagram (fragile)
- PLOT using free GNUPLOT software
- The software interface, OCASI, has the basic routines
- Parallel calculation of many multi-component equilibria using OpenMP
- Assessment of model parameters

Current status

What is still in the pipeline:

- More models are waiting to be implemented
- Assessment works but there are many utilities missing
- OCASI has to be restructured.
- Improving convergence and stability of calculations needed
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The best of all: Everyone interested can participate.

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- Bo Sundman, Ursula R Kattner, Mauro Palumbo and Suzana G Fries, *OpenCalphad - a free thermodynamic software*, Integr Materials and Manufact Innovation, **4**:1 (2015)
- Bo Sundman, Xiao-Gang Lu and Hiroshi Ohtani, *The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software*, in Comp Mat Sci, **101** (2015) 127-137
- Bo Sundman, Ursula R Kattner, Christophe Sigli, Matthias Stratmann, Romain Le Tellier, Mauro Palumbo, Suzana G Fries; *The OpenCalphad thermodynamic software interface*, Comp Mat Sci **125** (2016) 188-196

