Calphad databases, heat capacities and the liquid 2-state model

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Outline

- Calphad and the first generation databases
- Second generation Calphad databases
- Third generation Calphad databases
- Unary liquids and the glass transition
- OpenCalphad software

Calphad

In 1973 Larry Kaufman together with a few interested scientists, including Mats Hillert (Sweden), Himo Ansara (France), Philip Spencer (Germany) and Pieter Miodownik (UK) created a non-profit organisation called Calphad (CALculation of PHAse Diagrams) with the aim to develop software and databases to calculate phase diagrams for alloys from their thermodynamic properties.

Lattice stability concept

Larry Kaufman is the father of the "lattice stability" concept which means assigning a Gibbs energy of formation to all possible crystal structure of an element A, even for structures that are not stable for that element.

$$G_{\mathrm{A}}^{\alpha} - G_{\mathrm{A}}^{\beta} = a + bT \tag{1}$$

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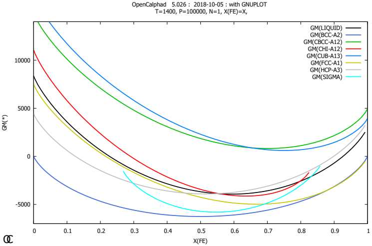
For example Chromium is never stable with the fcc structure and before the introduction of a lattice stability for fcc-Cr everyone used different descriptions of fcc-Cr when it dissolved in fcc-Fe, fcc-Ni or fcc-Pt.



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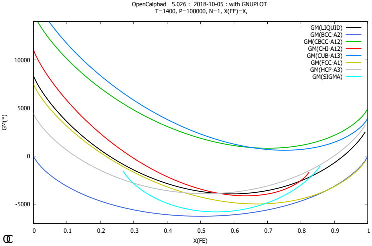
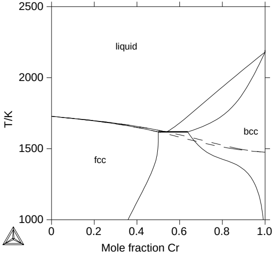
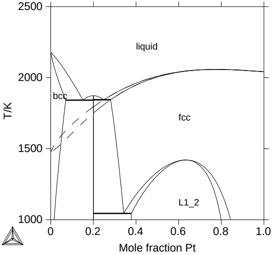


But to calculate multicomponent alloys it is necessary that an element has the same lattice stability when dissolved in the same phase in all binary systems.

Lattice stability concept

In some cases Larry Kaufman could estimate a melting temperature of an element by extrapolating the liquidus curves as in these figures for fcc-Cr.

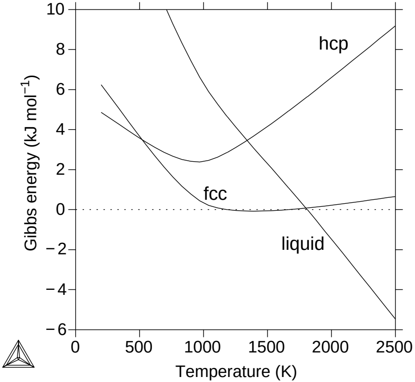




Together with an estimated entropy of melting that gives a lattice stability for fcc-Cr.

Lattice stability concept

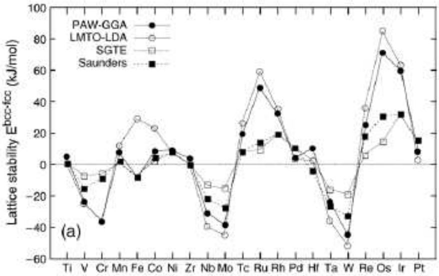
Some elements have non-linear lattice stabilites and to estimate the difference in the Gibbs energy for fcc, bcc, hcp and liquid for pure Fe, Larry Kaufman used the rudimentary first principles technique available at that time and he could estimate curves like this.



These curves show the Gibbs energies for fcc, hcp and liquid relative to bcc. The reason the lattice stabilities are non-linear is the ferromagnetic transition of bcc iron (ferrite).

Lattice stability callenge

But in 1984 Hans Skriver published lattice stabilty calculations at 0 K based on first principles methods that for some elements deviated considerably from the Calphad values.



The open circles are from Skriver in this figure published 2004 by Y Wang et al in Calphad, **28** (2004) pp 79-90.

Lattice stability callenge

But in 1984 Hans Skriver published lattice stabilty calculations at 0 K based on first principles methods that for some elements deviated considerably from the Calphad values.
This created some doubts on the Calphad technique but the problem was solved by discovering that the values calculated by Skriver were “mechanically unstable”. His fcc-Cr is not stable relative a Bain-transformation.

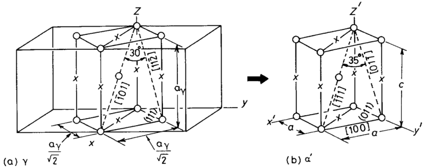


Fig. 6.7 Bain correspondence for the $\alpha \rightarrow \alpha'$ transformation. Possible interstitial sites for carbon are shown by crosses. To obtain α' the γ unit cell is contracted about 20% on the *C* axis and expanded about 12% on the *a* axes.

In 1984 one could not relax the structures in a DFT calculation.
A recent paper by Axel van der Walle at al. in Calphad, **58** (2017) pp 70-81 using DFT calculaions to develop a HEA database generally confirm the lattice stabilities from Larry Kaufman.

Second generation software and databases

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Including heat capacity data made the Calphad databases useful for many more applications in process modelling, simulations of phase transformations, energy conversion etc.

Low T limit

The lower limit for the heat capacities in the 1991 Calphad databases was set to 298.15 K in accordance with the existing substance databases like JANAF and Barin and Knacke.

Another reason was also that almost all applications of the Calphad technique deal with phase transformation and below 300 K such transformations are very slow because diffusion is slow.

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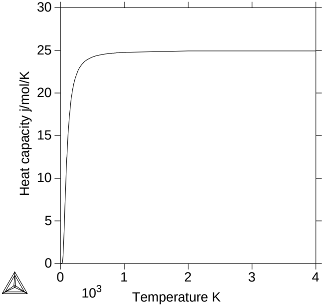
But there is a growing interest to extend the heat capacity model down to 0 K as many physicists are now making DFT calculations at 0 K and also calculate phonon spectra to obtain heat capacity data.

Low T limit

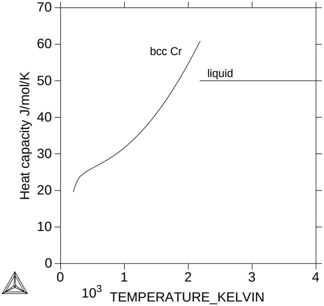
The vibrational heat capacity in a solid follows the Dulong-Petit rule at high temperature and the Debye function at low temperature.



Wikipedia: “Although the Einstein model of the solid predicts the heat capacity accurately at high temperatures it noticeably deviates from experimental values at low temperatures. See Debye model for how to calculate accurate low-temperature heat capacities.”

Low T limit

But real materials deviates significantly from the Dulong-Petit rule at high T like pure Cr, here calculated from the SGTE unary database:



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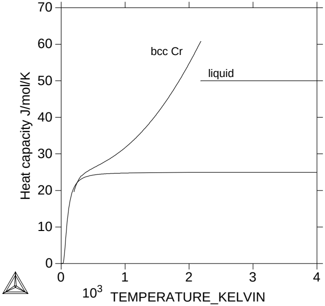
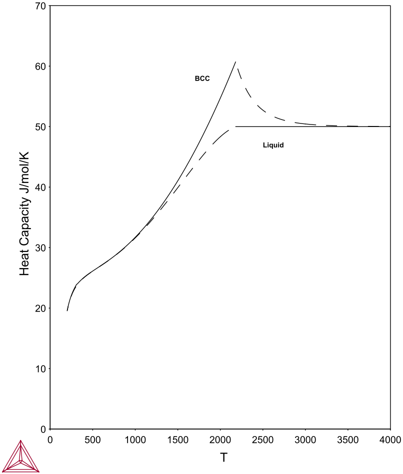


Here together with the Einstein solid model.

Breakpoint at melting *T*

In the SGTE unary the heat capacity curves for pure Cr are extrapolated (dashed) in the metastable ranges of bcc and liquid.



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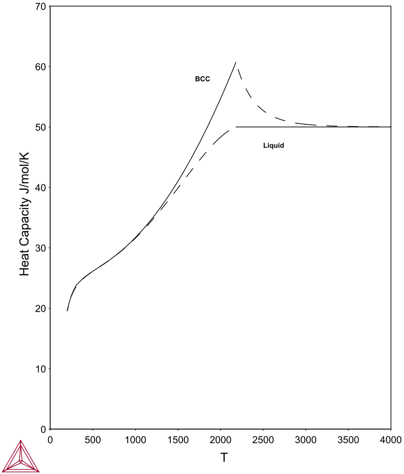

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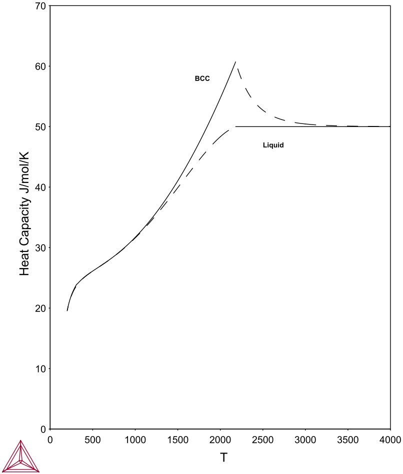

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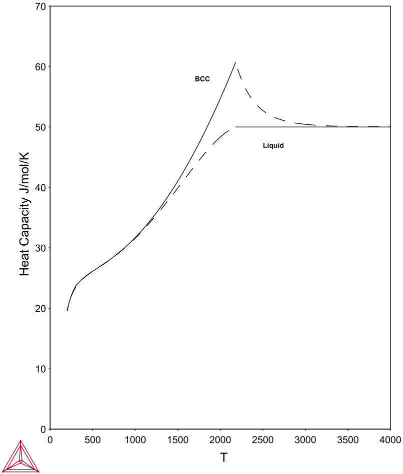

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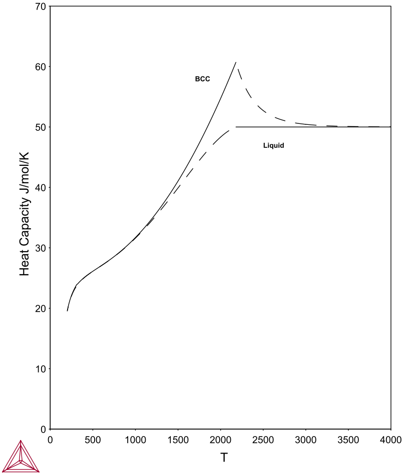

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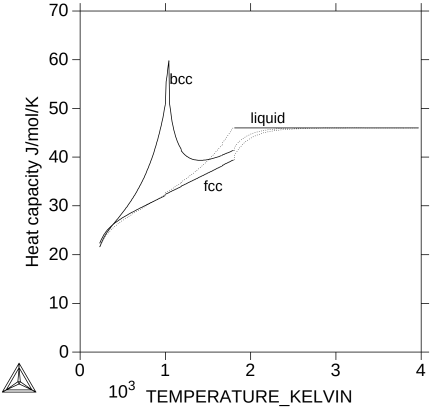
- It is also a problem (at least for geologists) that the breakpoint is a fixed value and does not vary with P.

Another pure element

Here are the stable and extrapolated heat capacity curves and magnetism for the different forms of pure Fe.



So there is still a lot of theory to develop to match reality

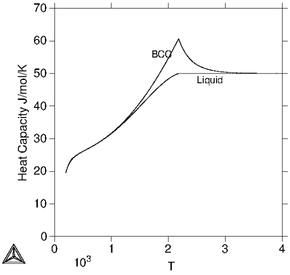
Workshop about pure element data

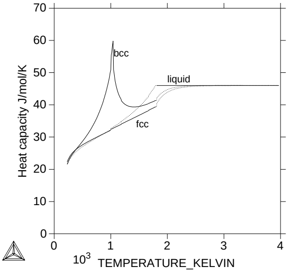
In 2013 there was a Ringberg workshop about the unary database taking into account the last 25 years of improved hardware, software, experimental techniques, first principles calculations etc. published in Physica Status Solidi (B) Vol 251, issue 1, (2014):

- Hickel et al., Computational Thermodynamics: Recent developments and future potential and prospects. pp 9-13
- Palumbo et al., Thermodynamic modelling of crystalline phases. pp 14-32
- Becker et al., Thermodynamic modeling of liquids, pp 33-52
- Körman et al., Lambda transitions, pp 53-80
- Hammerschmidt et al., Including effects of pressure and stress, pp 81-96
- Rogal et al., Perspectives on point defect thermodynamics, pp 97-129

3 tasks for the 3rd generation unary database

1. The first task is to extend the low T limit for the Gibbs energy functions from 298.15 K to 0 K.
2. The second task is to eliminate the break point in the properties when extrapolating the liquid below the solidification T.
3. The third task is to eliminate the break point in the properties when extrapolating crystalline phases above the melting T.





General acceptance

But the most important issue developing a new unary database is that it will be universally accepted as was the case with the 1991 SGTE database.

When developing multicomponent solution databases it is very important that everyone in the whole world uses the same unary data because such databases are made by combining assessments from France, China, USA, Sweden etc. The interaction parameters determined in these assessments to describe solution phases depend strongly on the unary data.

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If scientists in France will start to use a different description of fcc-Cr than scientists in Germany, the Calphad technique will die because no country or group can by itself develop models and parameters for a reliable multicomponent solution database.

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Task 1, heat capacity down to 0 K

This is taken care of using an Einstein function and a polynomial in T **with no T and $T\ln(T)$ terms** to make $C_P = S = 0$ at $T = 0$ K.

$$^{\circ}G_{\mathrm{A}} = {}^{\mathrm{Ein}}G(\theta_{\mathrm{A}}) + a + bT^2 + cT^5 + \cdots + {}^{\mathrm{mgn}}G_{\mathrm{A}}(T_C, Bohr) \tag{2}$$

where ${}^{\mathrm{mgn}}G_{\mathrm{A}}$ is the magnetic term and θ_{A} the Einstein T in:

$$^{\mathrm{Ein}}G_{\mathrm{A}} = 3RT\ln(1 - \exp(-\frac{\theta_{\mathrm{A}}}{T})) \tag{3}$$

where R is the gas constant. The coefficients a, b etc. are fitted to $S_{298}, H_{298} - H_0$ and experimental data for C_P for the stable phase up to its melting point.

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- Phases which are stable at $T = 0$ K but **not perfect crystals**, like inverse spinel and alloys, can have $S \neq 0$.
- Phases which are **metastable** at $T = 0$ K can have $C_P \neq 0$ and $S \neq 0$ at $T = 0$ K.

Task 2, the liquid extrapolation

At the Ringberg meeting 2013 the so called **liquid 2-state model** was adopted for extrapolating the liquid phase below its solidification T.
The Gibbs energy for the 2-state model is given by

$$^\circ G_{\mathrm{A}}^{\mathrm{liq}} = G_{\mathrm{A}}^{\mathrm{am}} - RT\ln(1+\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT})) \tag{4}$$

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At low T we must have $G^{\mathrm{2state}} >> RT$ (which means $\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT}) \approx 0$):

$$^\circ G_{\mathrm{A}}^{\mathrm{liq}} = G_{\mathrm{A}}^{\mathrm{am}} = {}^{\mathrm{Ein}}G(\theta_{\mathrm{A}}^{\mathrm{am}}) + a + bT^2 + \cdots \tag{5}$$

where ${}^{\mathrm{Ein}}G$ is the Einstein function (eq. 3 above), $\theta_{\mathrm{A}}^{\mathrm{am}}$ is the Einstein T of the amorphous state and a, b are constants describing the the amorphous state stability relative solid phases including the melting T and melting enthalpy.

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In my opinion $G_{\mathrm{A}}^{\mathrm{am}}$ can have terms with T and $T\ln(T)$ as the amorphous state is metastable at $T = 0$ K and thus have non-zero S and C_P at $T = 0$ K but this is still discussed.

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At high T in the liquid state we must have $\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT}) >> 1$, i.e. eq. 4 becomes:

$$^\circ G_{\mathrm{A}}^{\mathrm{liq}} = G_{\mathrm{A}}^{\mathrm{am}} - RT\ln(\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT})) = G_{\mathrm{A}}^{\mathrm{am}} + G_{\mathrm{A}}^{\mathrm{2state}} \tag{6}$$

where G^{2state} is a polynomial in T:

$$G_{\mathrm{A}}^{\mathrm{2state}} = c + dT + eT\ln(T) + \cdots \tag{7}$$

where c, d, e etc. are constants fitted to the properties of the stable liquid and the transition T from the amorphous to liquid state.

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where $G_{\mathrm{A}}^{\mathrm{am}}$ describe the low T metastable amorphous state and $G_{\mathrm{A}}^{\mathrm{2state}}$ the difference between the stable liquid and the amorphous state.
The intermediate range of T when we have the transition from amorphous to the liquid state is very sensitive to the $G_{\mathrm{A}}^{\mathrm{2state}}$ function. The transition occur when $\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT} \approx 1$.
The rate of change of $\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT}$ with T around this value has a big influence how the thermodynamic properties varies during the transition from the amorphous to the stable liquid phase.

Task 2, example

Take a very simple case:

- the Einstein $\theta_{\mathrm{A}}^{\mathrm{am}} = 300$
- the stable liquid should have a constant heat capacity of 50 J/mol/K.

As we have already $C_P = 3R \approx 24.94$ J/mol/K from the ${}^{\mathrm{Ein}}G(\theta_{\mathrm{A}}^{\mathrm{am}})$ we include the extra 25 J/mol/K in:

$$G_{\mathrm{A}}^{\mathrm{2state}} = c + dT - 25T\ln(T)$$

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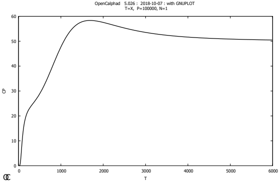
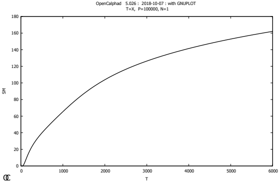
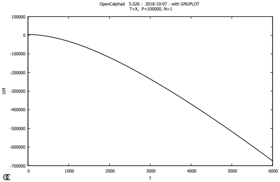
$G^{\mathrm{2state}} = 100 + 180T - 25T\ln(T)$:







Task 2, example

Take a very simple case:

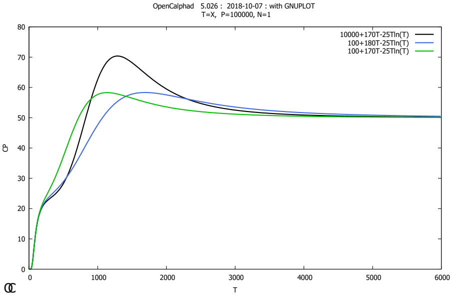
- the Einstein $\theta_{\mathrm{A}}^{\mathrm{am}} = 300$
- the stable liquid should have a constant heat capacity of 50 J/mol/K.

As we have already $C_P = 3R \approx 24.94$ J/mol/K from the ${}^{\mathrm{Ein}}G(\theta_{\mathrm{A}}^{\mathrm{am}})$ we include the extra 25 J/mol/K in:

$$G_{\mathrm{A}}^{\mathrm{2state}} = c + dT - 25T\ln(T)$$

- The values c and d can be selected in order to have a smooth heat capacity for the transition from amorphous to liquid state below the melting T, here assumed to be around 2000 K.

The “hump” shape and position changes with the c, d coefficients.



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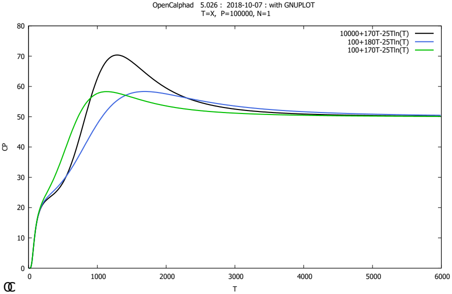


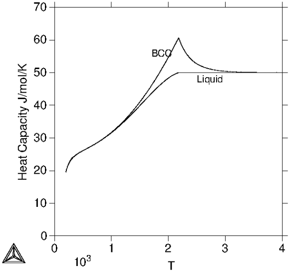
There will always be a “hump”.

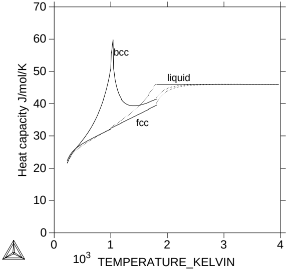
With a smaller d coefficient and larger c the “hump” maximum will grow.

With smaller C_P term the d coefficient will be less positive.

Task 3, extrapolation of solids

There is still no accepted way to eliminate the break point in the Gibbs energy of the solid above the melting T. Most solids have a more or less steeply increasing heat capacity before melting and extrapolating this will make the solid stable again at high T.
There is a suggestion to use the quotient of the entropy of the solid and the entropy of the liquid to prevent to solid to become stable again but this is still discussed.





OpenCalphad - objectives

The OpenCalphad (OC) is an informal collaboration between scientists interested in developing a free high quality thermodynamic software. At present OC provides:

- a platform to implement and test new thermodynamic models,
- a fast and reliable algorithm for equilibrium calculations,
- facilities to calculate property and phase diagrams,
- possibilities to assess model parameters and develop assessment techniques,
- a software interface for integration in materials simulation programs.

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- a software interface for integration in materials simulation programs.

Additionally OC can calculate equilibria in parallel.

Current release is available at http://www.opencalphad.org
with a fairly extensive documentation and user guide

Current development status

What is working:

- Compound Energy Formalism (CEF) and ionic liquid models
- Magnetic and order/disorder models
- Reading (unencrypted) TDB files and entering data interactively
- Command line oriented user interface with macro facilities
- Many different types of conditions, also relations between state variables
- Calculating multicomponent equilibria
- STEP calculation of property diagram
- MAP of binary, ternary and multicomponent phase diagram
- PLOT using GNUPLOT software
- The software interface, OCASI, is stable and flexible
- OC/OCASI can calculate multicomponent equilibria in parallel
- Assessment of model parameters

Current development status

What is still in the pipeline:

- More models in particular for unaries and short range ordering.
- A PhD student is improving the assessment module.
- Improving convergence and stability of calculations.
- The documentation needs better structuring.

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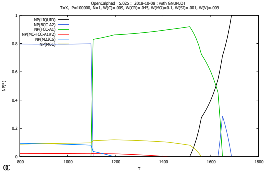
The best of all: the code is free so anyone interested can participate.

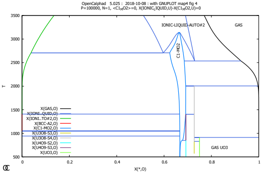
A development version updated a few times each month can be downloaded from http://www.github.org/sundmanbo/opencalphad

To install OC you need to know how to compile a software and you must have your own databases or find them elsewhere.

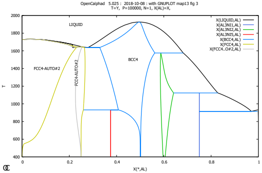
Some diagrams calculated by OC



(a)



(b)



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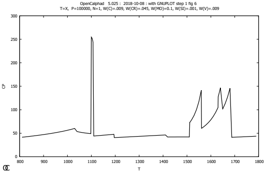

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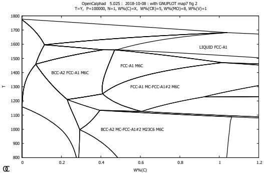

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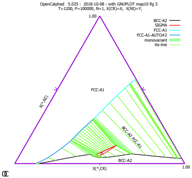

(f)

Thanks for listening