

Phase Transformations from Thermodynamics

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Thermodynamics

Thermodynamics is the science of the impossible.

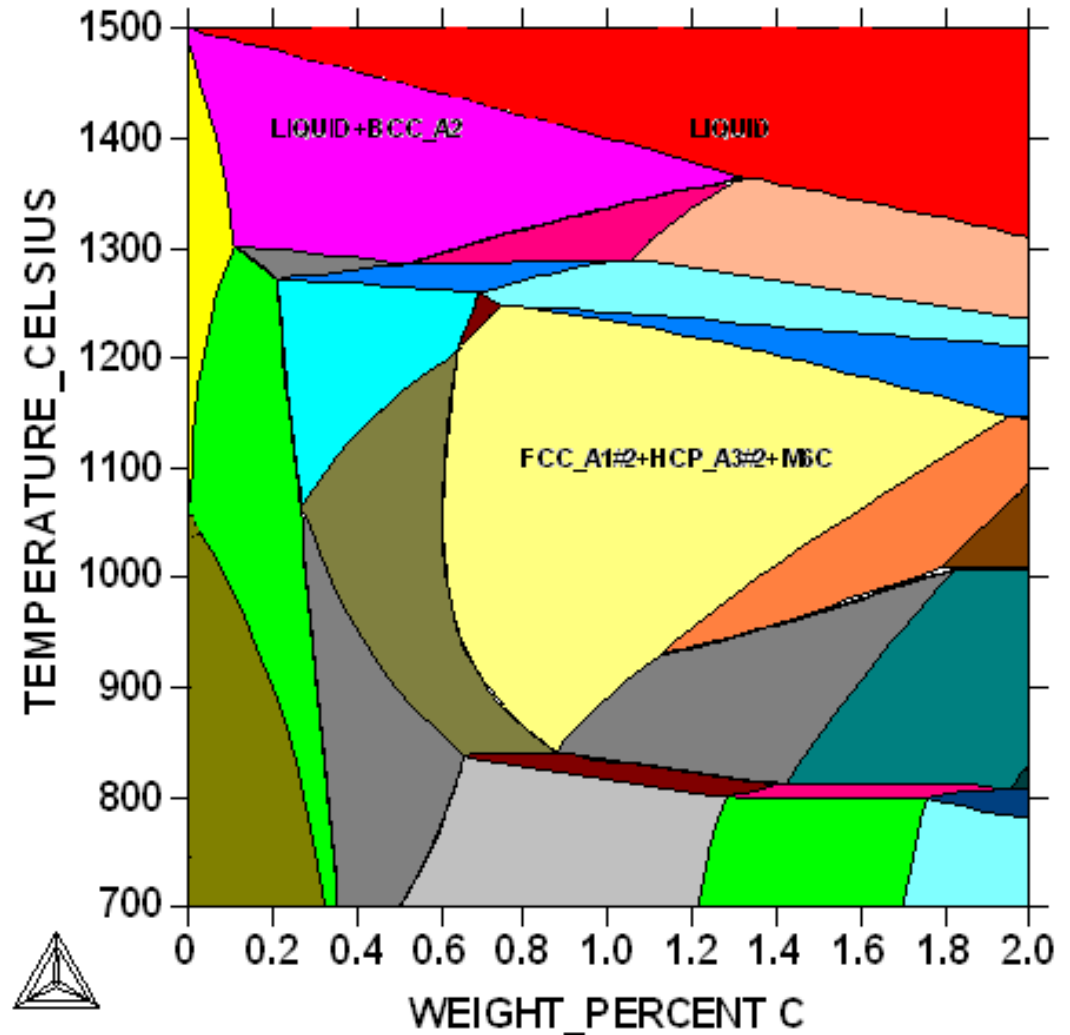
It can only tell you if a transformation or reaction is not possible. It can not tell you which of all possible transformations that will actually happen.

But even that is usually very good because you can then reduce the number of transformations proposed from physical theories to a few interesting ones.

Multi-component phase diagrams

A classical application of thermodynamics is the calculation of multicomponent phase diagrams using the Calphad technique.

The colourful diagram here is for a high speed steel. Each coloured area has a different set of stable phases.



Thermodynamic properties

Knowing the thermodynamic properties of each phase makes it possible to calculate chemical potentials and thermodynamic factors, which are needed for simulation of diffusion in phase transformations.

The Calphad models can also provide quantities outside the stable range of the phases which is necessary to simulate phase transformations.

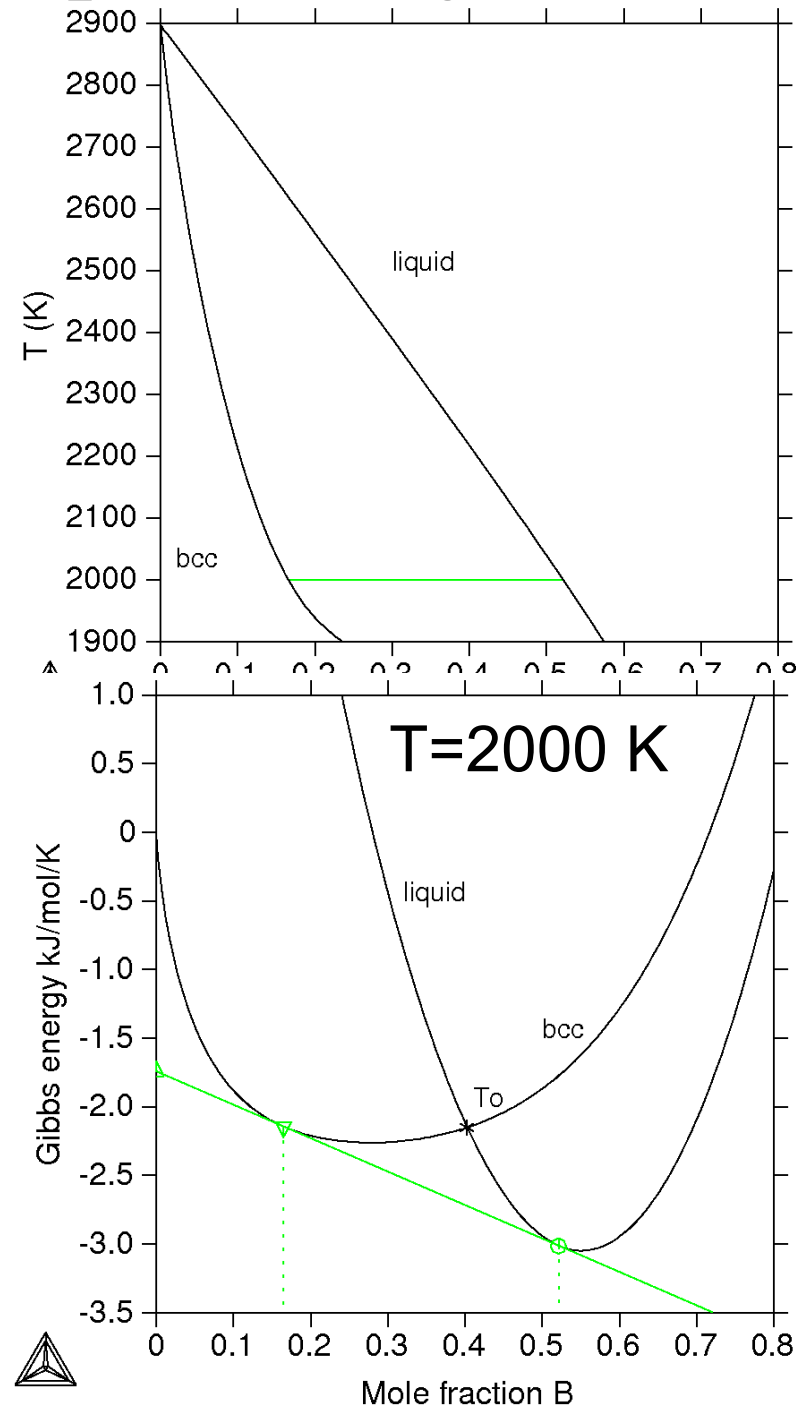
Such extrapolations from the stable state using the models are also useful to calculate the driving force for nucleation of a new phase.

Gibbs energy and phase diagram

The relation between the phase diagram and the Gibbs energy for each phase is illustrated by the "common tangent" construction shown as a green line in the figures for a binary system. The common tangent represent the stable state in the two-phase region.

For binary system this is trivial but with Calphad it can easily be extended to handle tangent hyperplanes connecting multi-dimensional Gibbs energy hypersurfaces in real alloys.

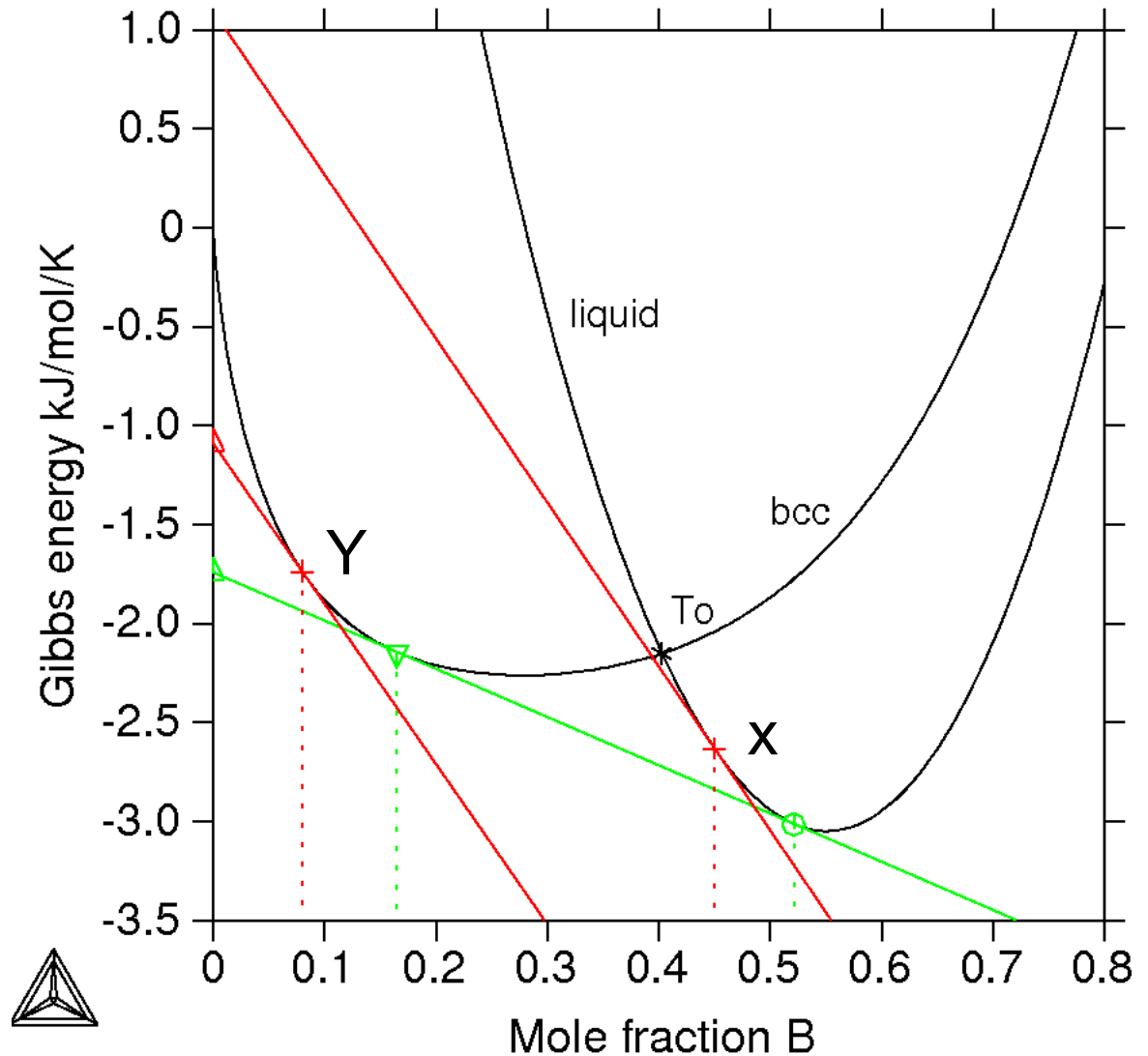
The tangent is also the chemical potential.



Metastable extrapolations of Gibbs energy

It is less well established to use the "parallel tangent" construction to obtain driving forces for nucleation and growth. This method makes use of the metastable extrapolation of the Gibbs energy for the liquid inside the two-phase region.

A liquid at **X** has a tangent as shown by the red line through X. The bcc phase at point **Y** has a parallel tangent and the highest driving force for nucleation. The green common tangent is the equilibrium.



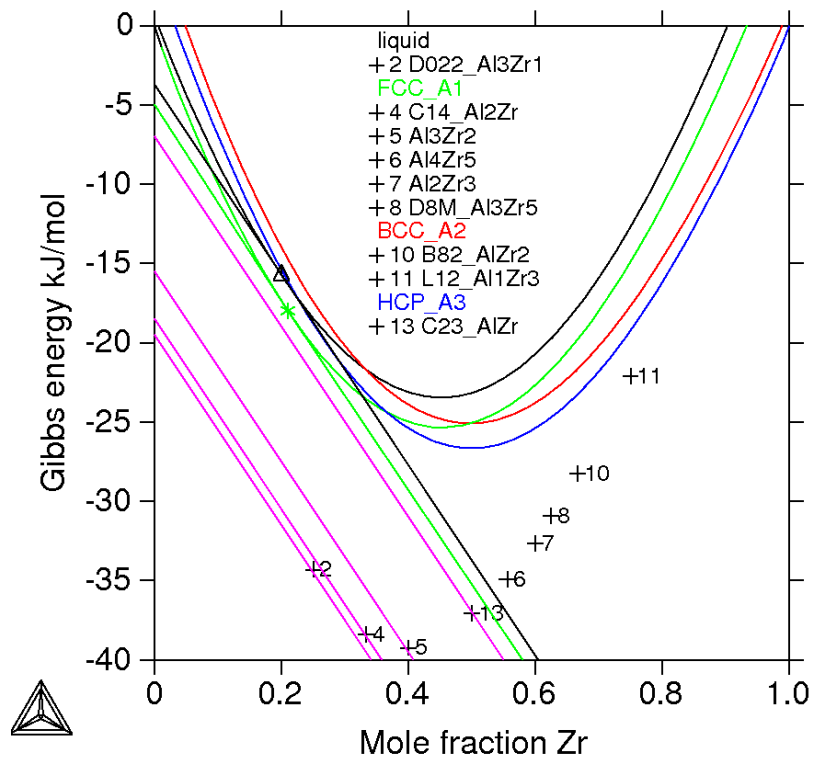
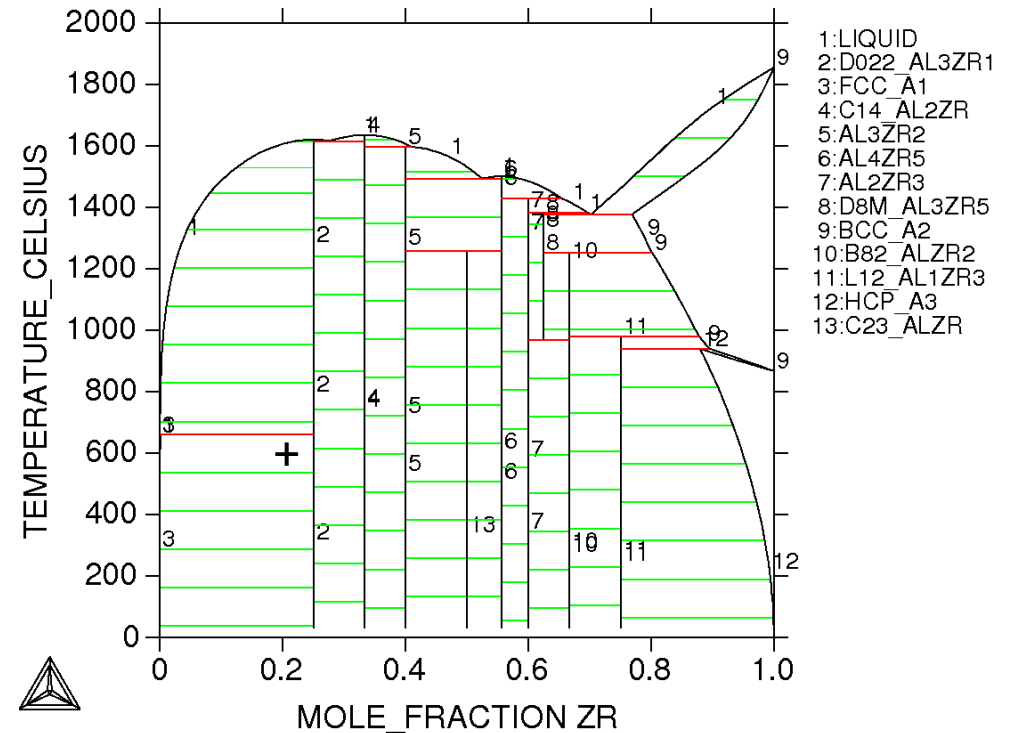
Plotting driving forces in the Al-Zr system.

The upper left diagram is the Al-Zr phase diagram.

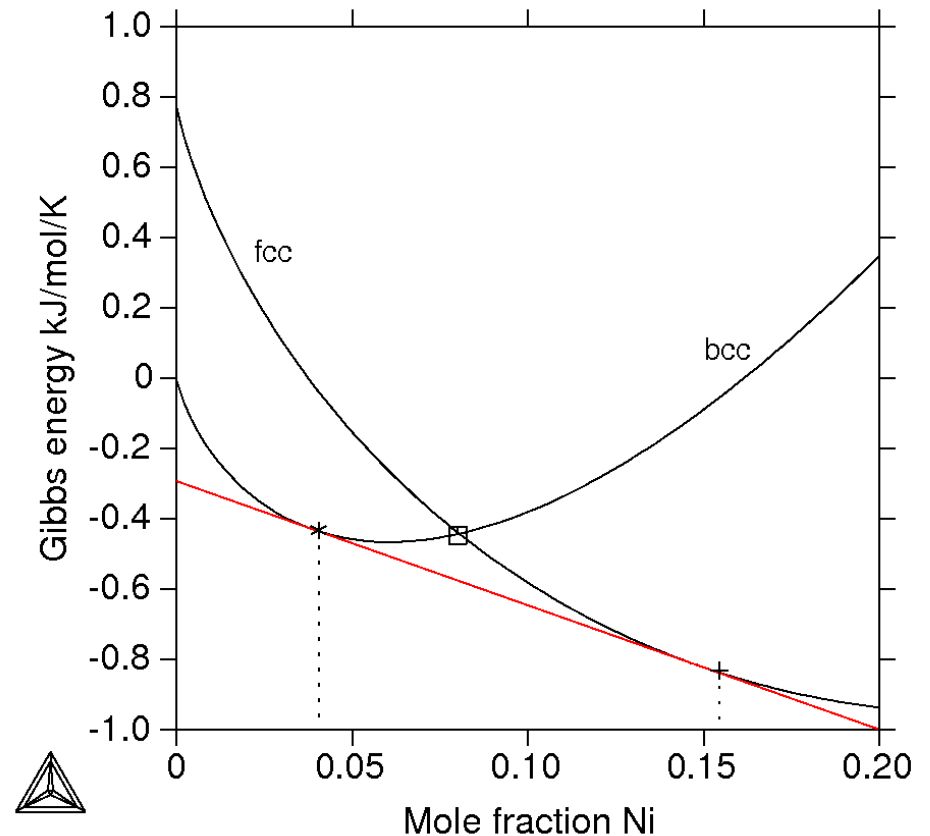
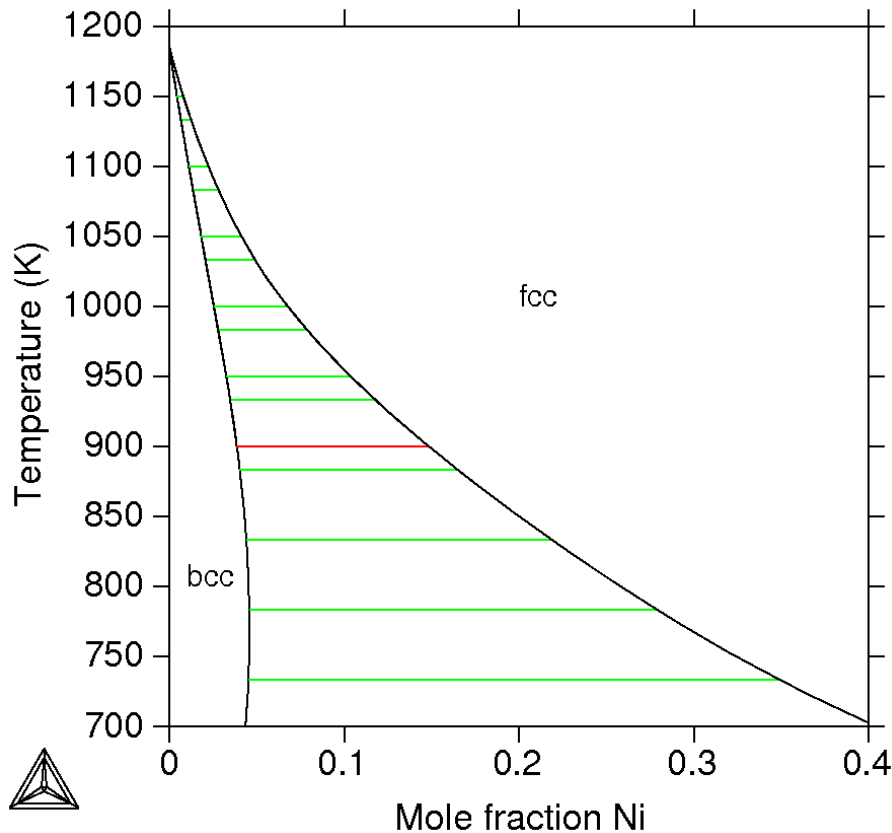
In the lower diagram the Gibbs energy curves at 600 °C are plotted together with the parallel tangents for a liquid phase with 20 at% Zr quenched to 600 °C (at the +). That requires very rapid cooling as such a liquid would like to precipitate D022_Al₃Zr already at 1600 °C.

The numbers represent the Gibbs energies of the compounds.

D022 has the highest driving force but for kinetic reasons any phase below the liquid tangent may form. One may even have a diffusionless transformation to a supersaturated fcc phase.



Phase diagram and Gibbs energy



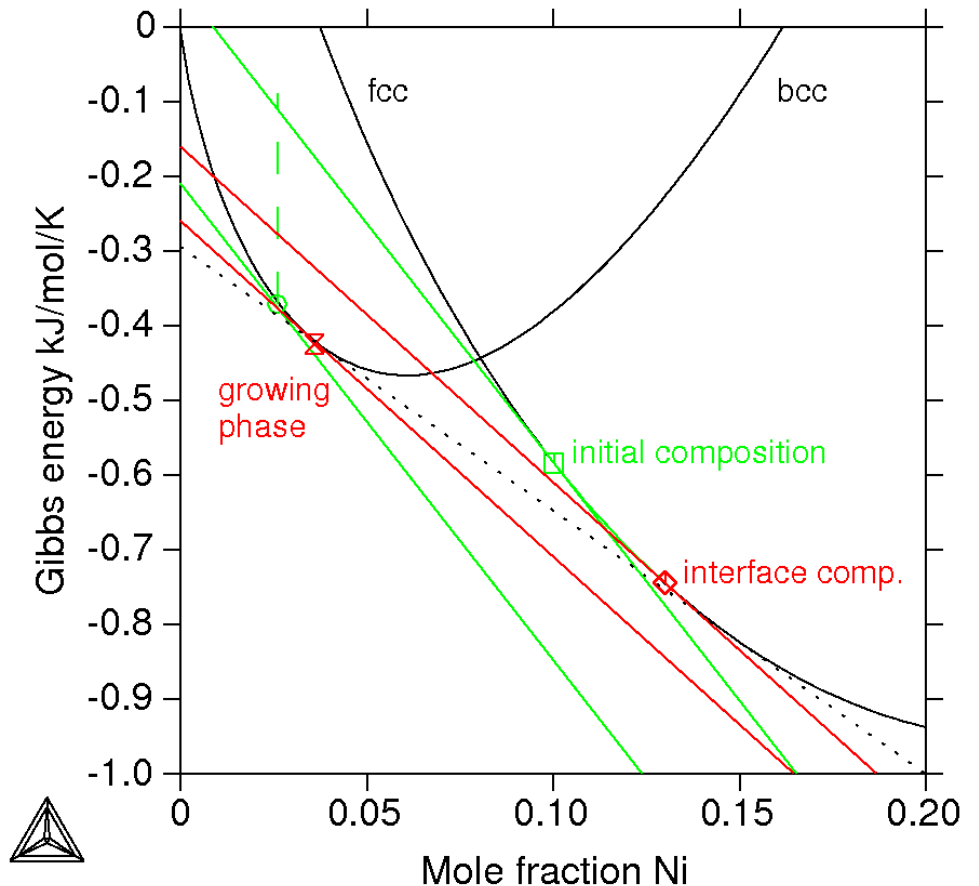
The phase diagram for Fe-Ni (left) calculated from the Gibbs energy functions for fcc and bcc. In the right figure these functions are shown at 900 K. The red line is the "common tangent" and the point where the curves cross is known as the "T₀" point

Nucleation and moving interfaces

Rapidly cooling an alloy with 10at% Ni to 900 K gives a meta-stable fcc at the green point. The green tangent to the fcc curve and the parallel green tangent constructed for the bcc curve gives the driving force for nucleation of bcc.

When the nucleus has started to grow there will be diffusion in the fcc phase and the parallel red tangents are a possible situation at the phase interface while it is moving. The final state is given by the dashed common tangent.

The position of the red tangents are governed by kinetic conditions.

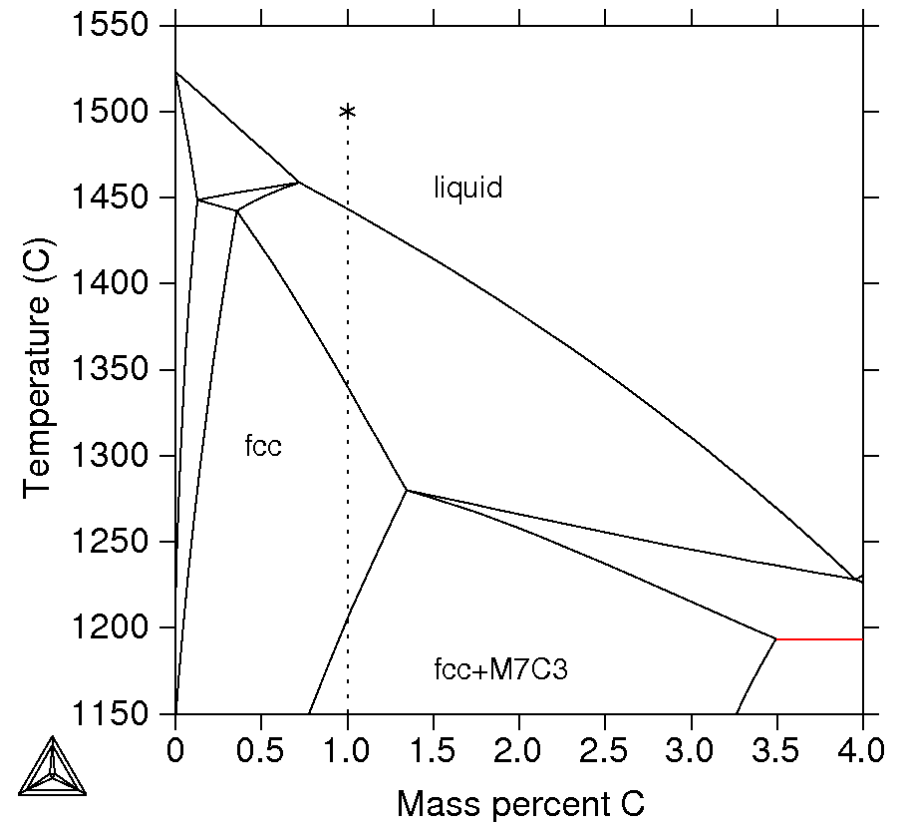


Scheil solidification simulation

The Scheil-Gulliver model for solidification need only thermodynamic data. It assumes no diffusion in the solid phases and infinitely fast diffusion in the liquid.

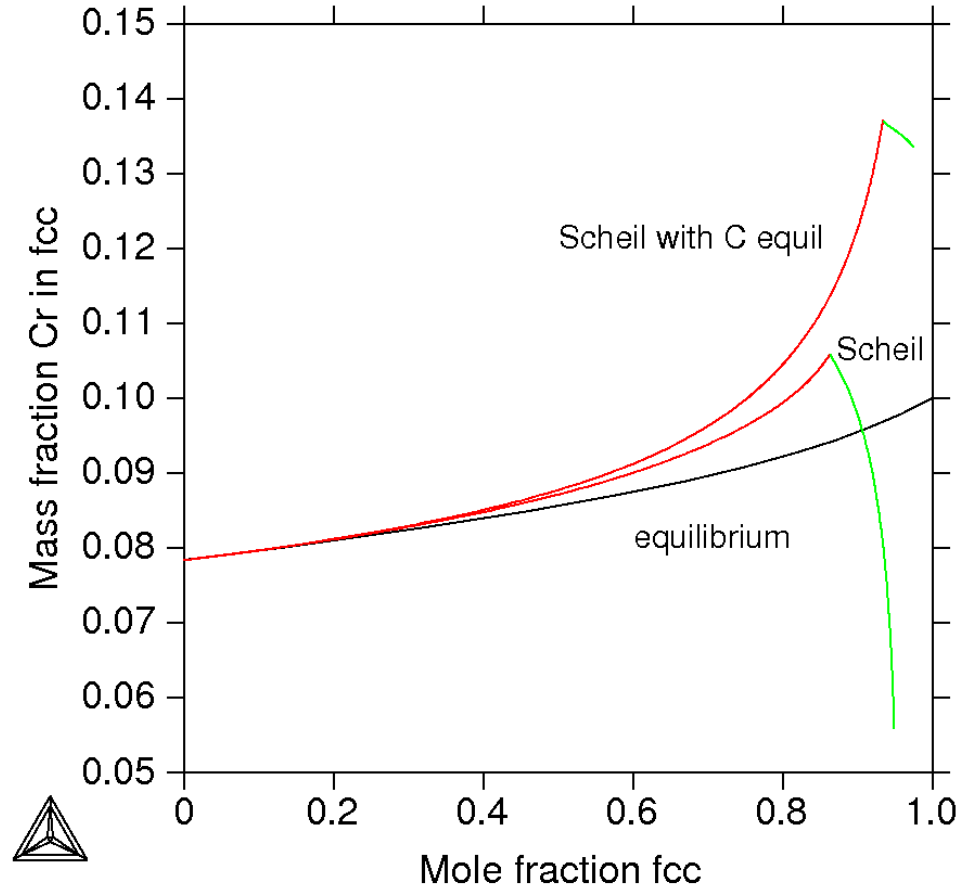
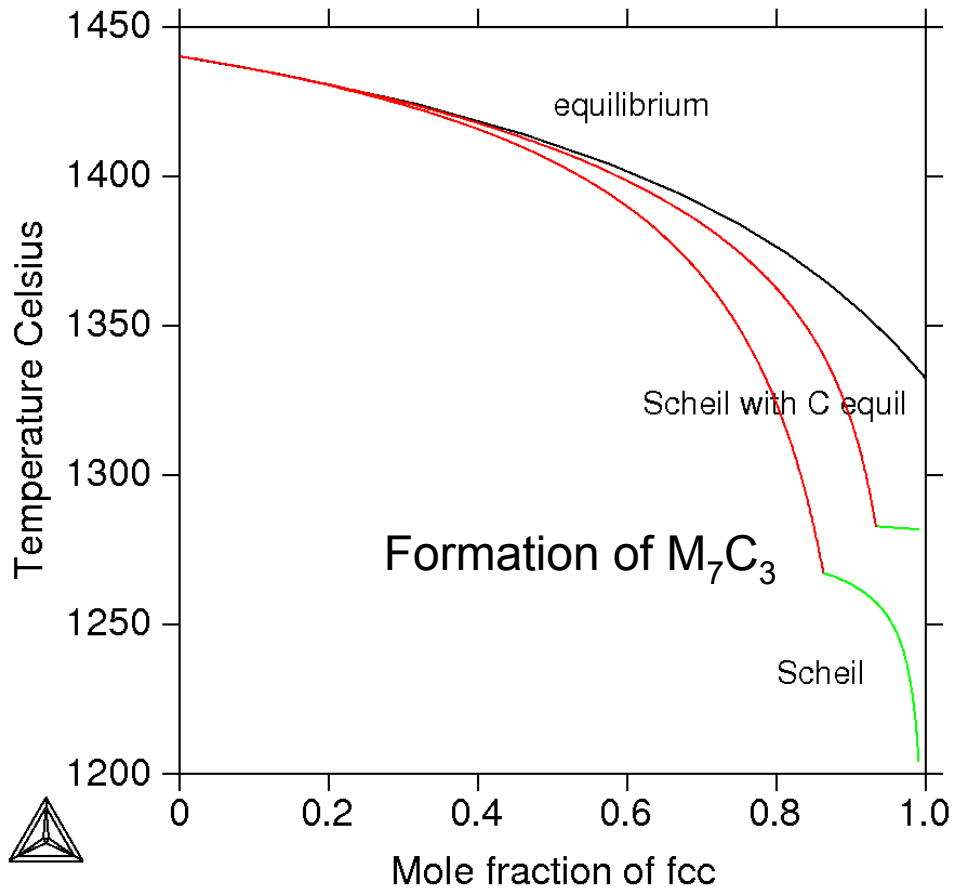
It has been used successfully to predict phases formed by segregation in aluminium alloys.

For solidification of steels one has the problem that C and N can diffuse very fast compared to the other elements. One thus need a modified Scheil model with equilibrium distribution of C and N between liquid and solid.



The isopleth phase diagram for C-10Cr-Fe. The dashed line represent the alloy. Without segregation it will solidify to fcc

Scheil solidification simulation with C



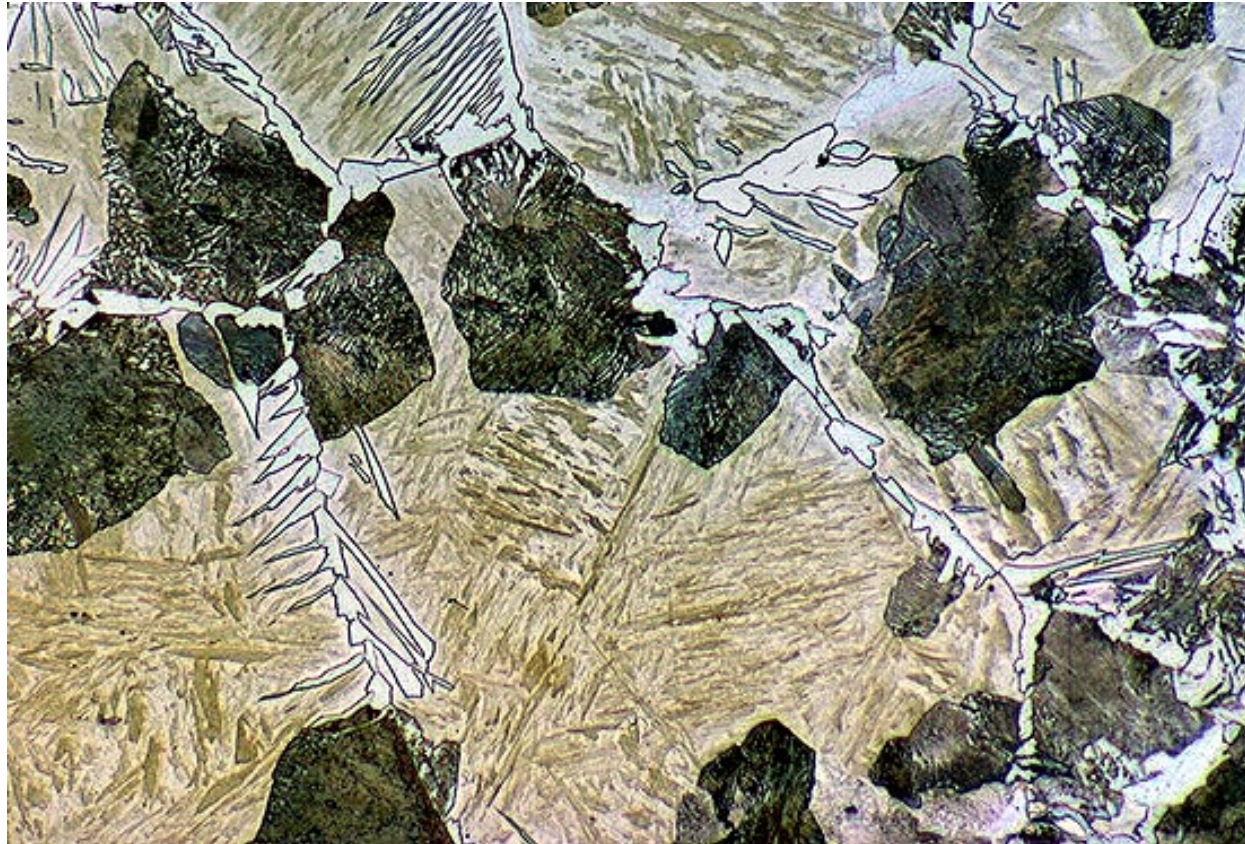
The simulations are for a steel with 10 % Cr and 1 % C. The left shows the solidification range for three simulations, the right the segregation of Cr for the same three cases. For the Scheil models the M_7C_3 carbide is formed.

Different diffusivities in solid state

In a steel one can have a phase transformation that is governed by diffusion of the interstitial components only and the growing phase inherits the same composition of the substitutional components.

This is the situation for transformations with the para-equilibrium and the Local Equilibrium Non-Partitioning (LENP) conditions. Some conclusions can be made for these without knowing the actual values of the diffusion coefficients.

Para-equilibrium ferrite



When austenite is cooled many things can happen as shown in this microstructure. Some of these require diffusion, some not. For an alloyed steel one can often assume that C and N have time to reach equilibrium at normal cooling rates but the alloying elements are immobile. That is para-equilibrium or LENP condition.

Para-equilibrium ferrite

The figure shows the stable iso-pleth phase diagram (black), the T_0 line (blue, the limit for diffusionless transformation) and the para-equilibrium lines for fcc transforming to bcc (red and green)

All these lines can be calculated from the thermodynamic models of the phases without any kinetic information.

The para-equilibrium gives how much ferrite can form with a fast reaction with only carbon redistribution.

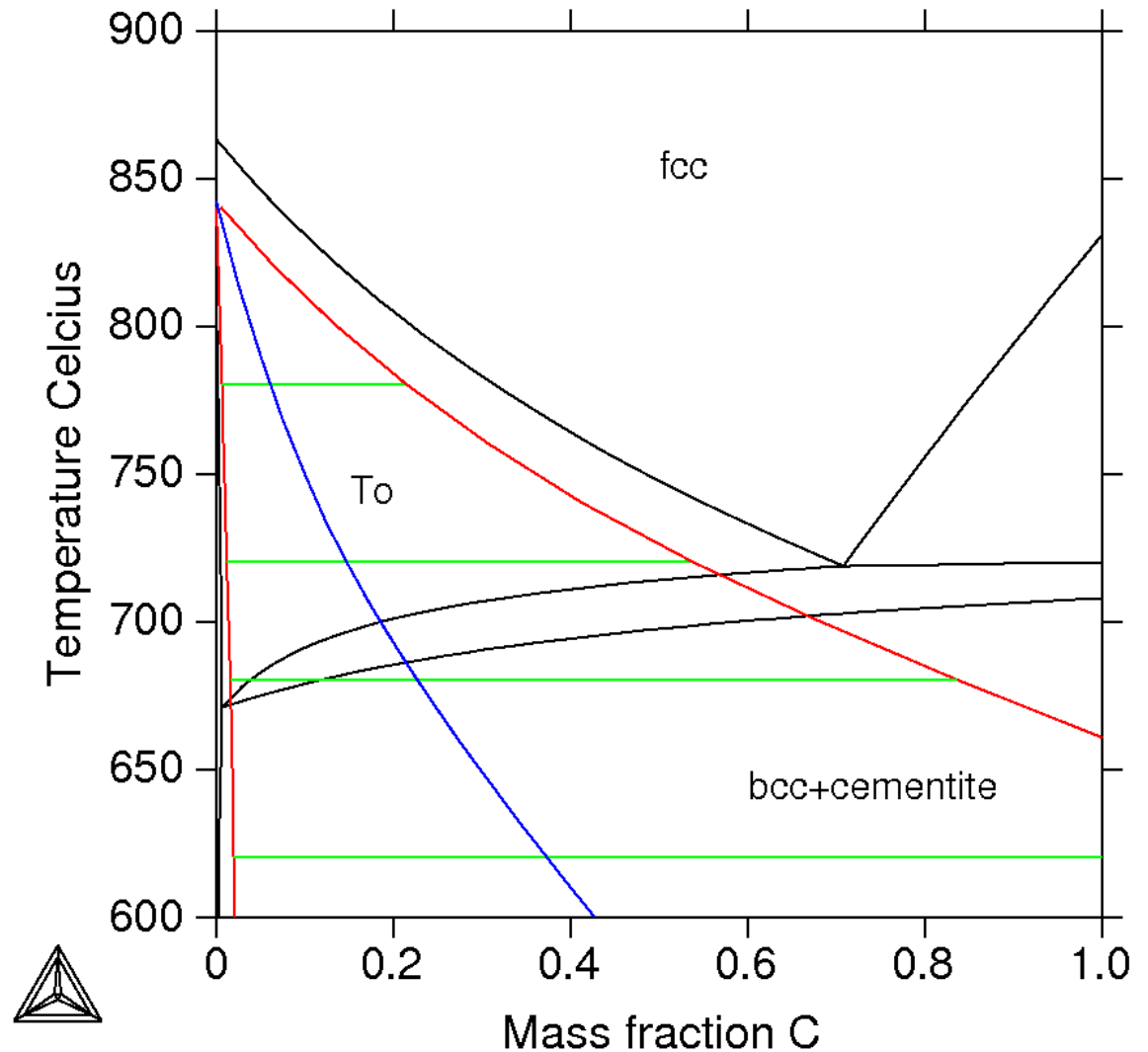


Diagram for a steel with 1.5% Mn, 0.3% Si

Isothermal para-equilibrium ferrite

An isothermal section at 727 C for the same steel. The black lines represent the stable phase diagram, the red lines the para-equilibrium diagram.

Note there are green tie-lines in the para-equilibrium diagram as the fcc and bcc must have the same fraction of the substitutional elements.

The Local Equilibrium Non Partitioning (LENP) gives similar results also using only thermodynamic data.

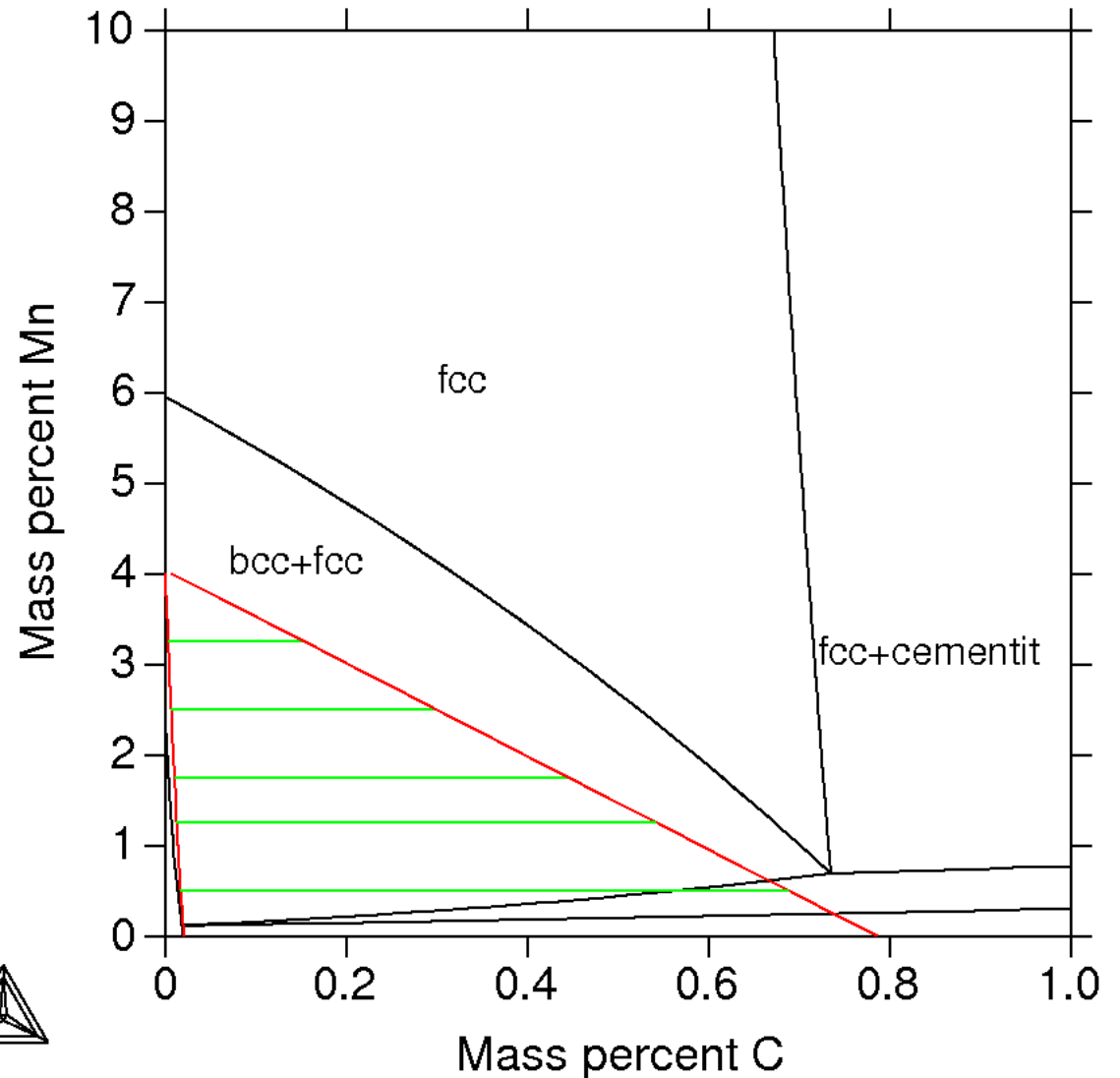
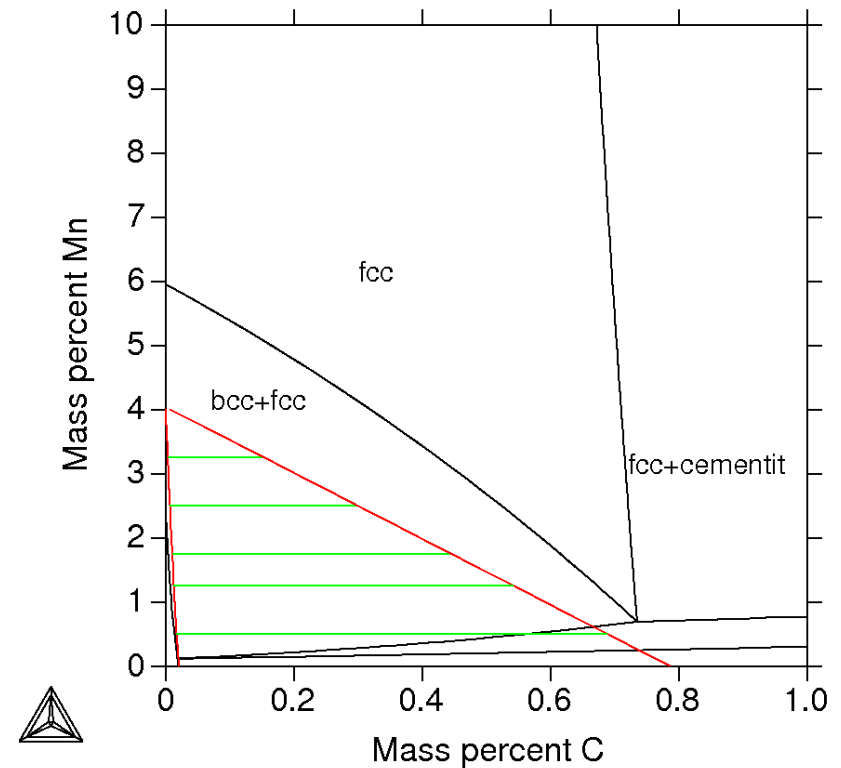
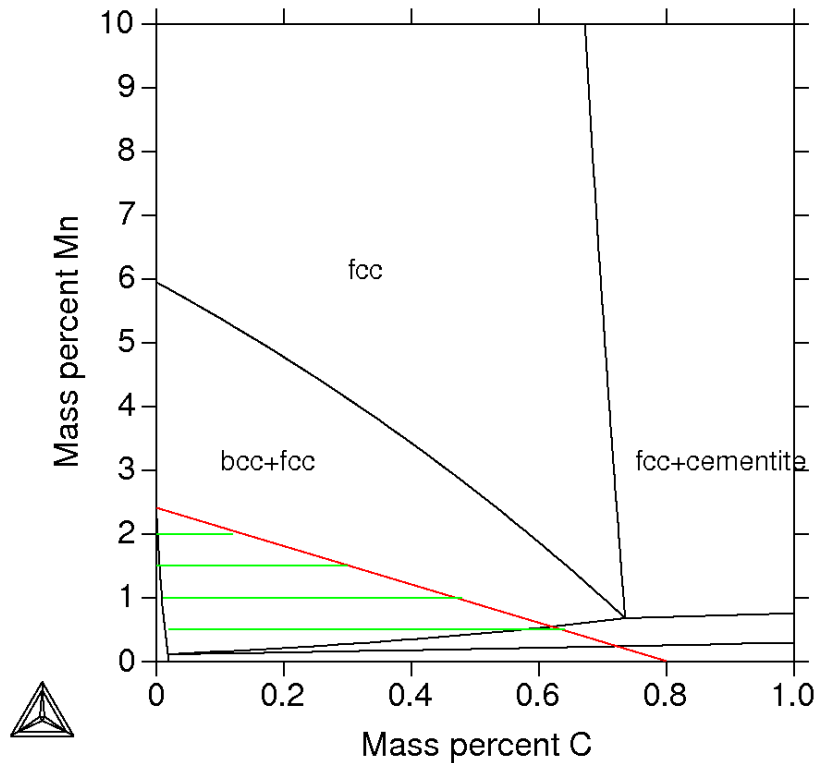


Diagram for a steel with 0.3%Si

Local Equilibrium Non-Partitioning



The LENP is very similar to para-equilibrium but one assumes there is an infinitely thin "spike" at the interface. This gives somewhat different driving forces and the left diagram is the "LENP" phase diagram for the same case as the right para-equilibrium diagram. Which one is the "correct" one can be judged from the amount of "fast" ferrite formed.

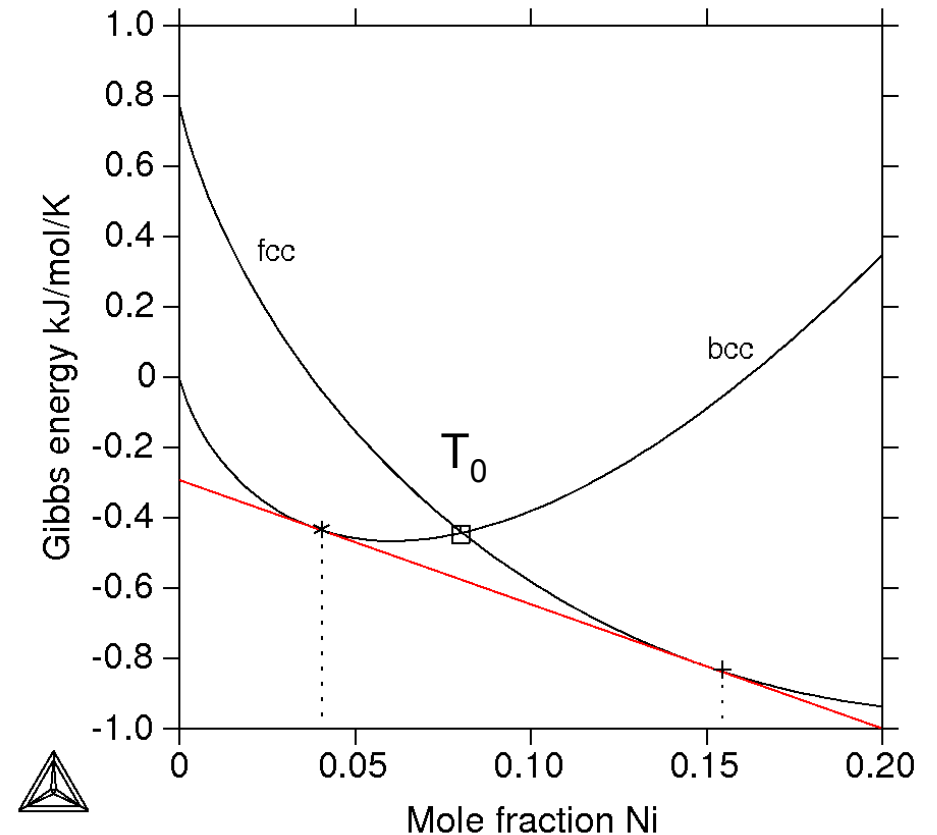
LENP algorithm

- Calculate equilibrium at given T and ferrite entered with the austenite alloy composition (except carbon) and with austenite fix with 0 moles.
- This gives a carbon activity at the ferrite/austenite interface and a carbon content of ferrite, x_C^α .
- Calculate the carbon content in the austenite, x_C^γ , using its original alloy composition and the carbon activity from the first calculation.
- If this carbon content is higher than the original carbon content in the austenite then LERP transformation is possible because carbon can diffuse from the interface into the austenite.
- The amount of "fast ferrite" according to LERP is given by the lever rule using the calculated carbon contents and the original carbon content of the austenite.

Diffusionless massiv transformation

Going back to the curves with the stable tangent one should note the point of intersection between the Gibbs energy curves, the T_0 point.

For Ni contents lower than this one can have a diffusionless transformation from fcc to bcc. If that will happen or not is determined by kinetic factors. The "solute drag" theory can be used to simulate 1D transformations varying from very slow to diffusionless based on the Gibbs energy curves and kinetic factors like interface mobilities.

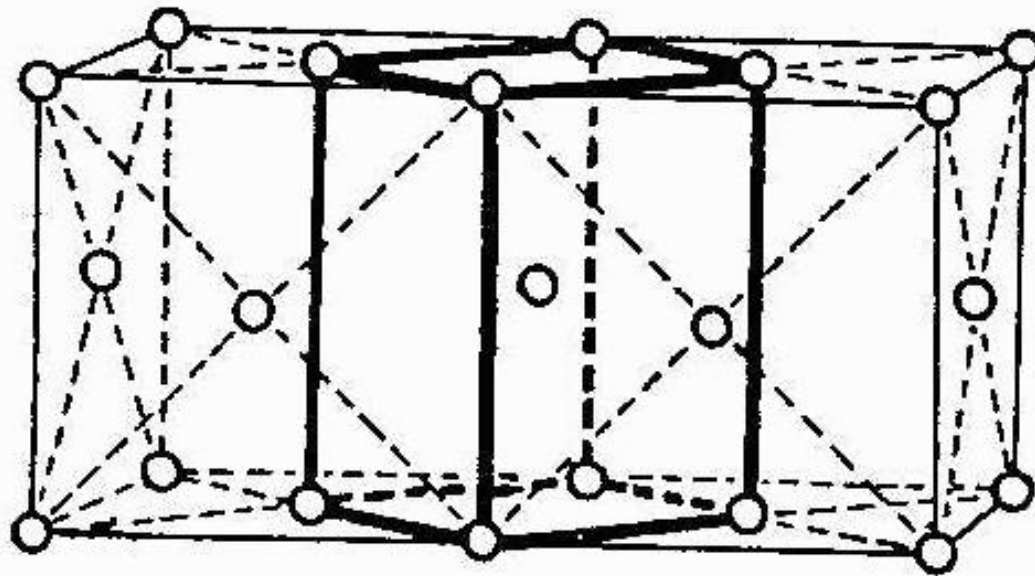


Martensite transformation

For the martensite transformation one must also be on the right side of the T_0 point but in addition the growth will only take place in certain crystallographic directions in the matrix phase where the surface energies have a low energy due to the lattices. Dislocations are generated to at the growing edge to accommodate the lattice mismatch.

Relation between FCC and BCC lattices

- The Bain displacement connect the fcc and bcc lattices
- The martensite transformation is a Bain displacement
- One can apply this to $L1_0$ also and transform $L1_0$ to B2
- There are a few systems with B2 and $L1_0$ ordering on top of each other (Mn-Ni).



Quality of extrapolations

- The usefulness of the extrapolated Gibbs energies depend how good the metastable ranges of the phases have been assessed. In fact they are surprisingly reasonable especially if rather simple models are used.
- In new assessments with more complex models the extrapolations can be quite wrong if the assessor is not aware of the importance of using thermodynamic functions outside the stable range.
- But many assessed systems need reassessments to have good extrapolations.
- Ab initio calculations are very important in order to have reliable extrapolations of the phases.

Reassessments : Al-Fe

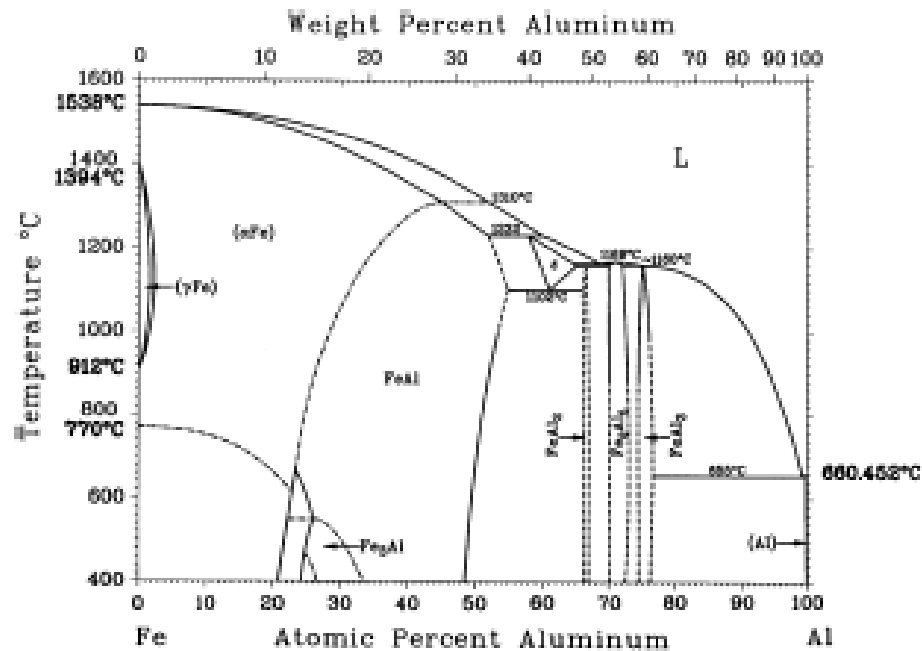
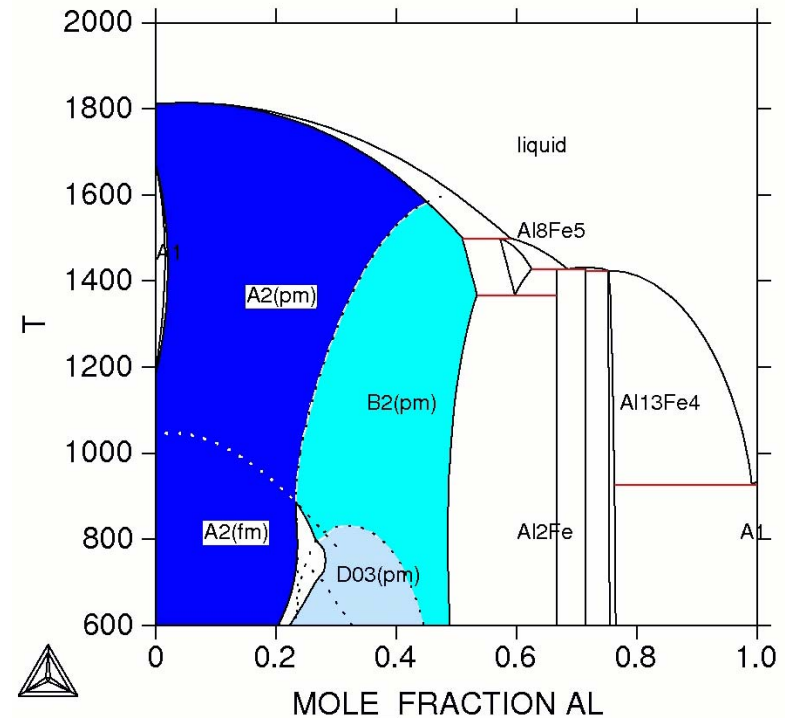
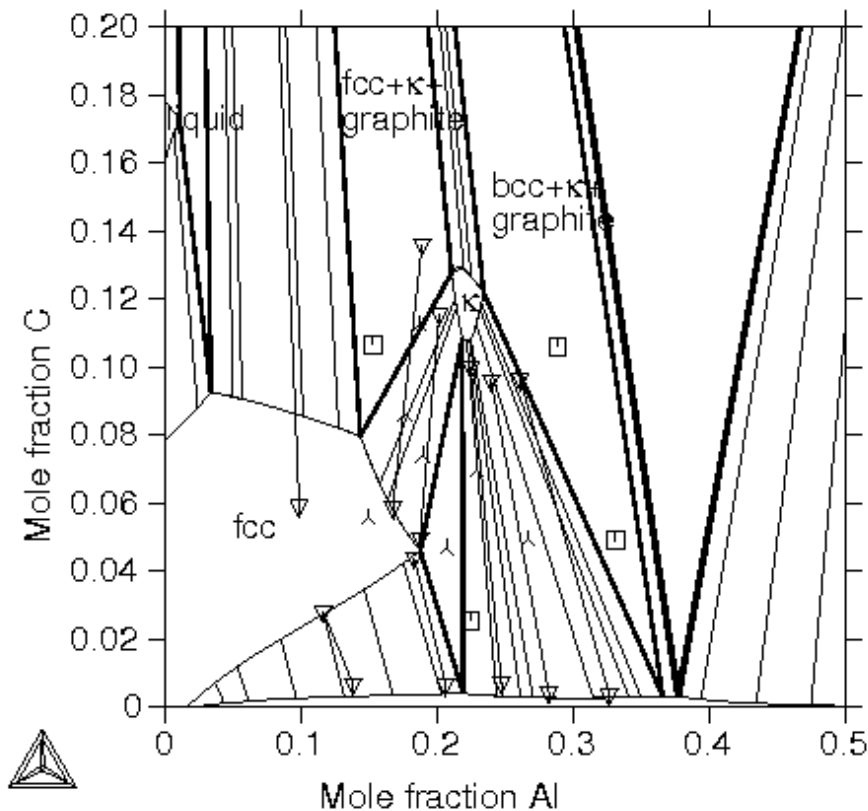


Fig. 2. The Fe-Al system according to the assessment by Kattner [48].

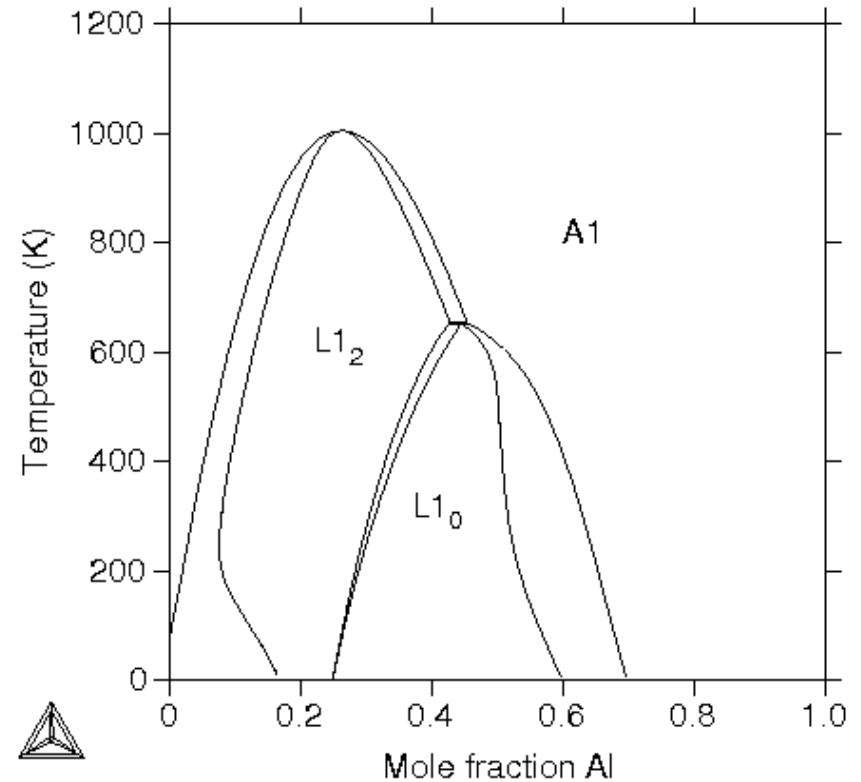


The Al-Fe system has both B2 and D0_3 ordering and both 1st and 2nd order transitions between these ordered states. In addition there is a ferromagnetic transition which depends on composition and the ordered state. With the 4 sublattice model these transformations can be described reasonably well.

Re+assessments: Al-C-Fe



Extention of fcc in Al-C-Fe at 1473 K

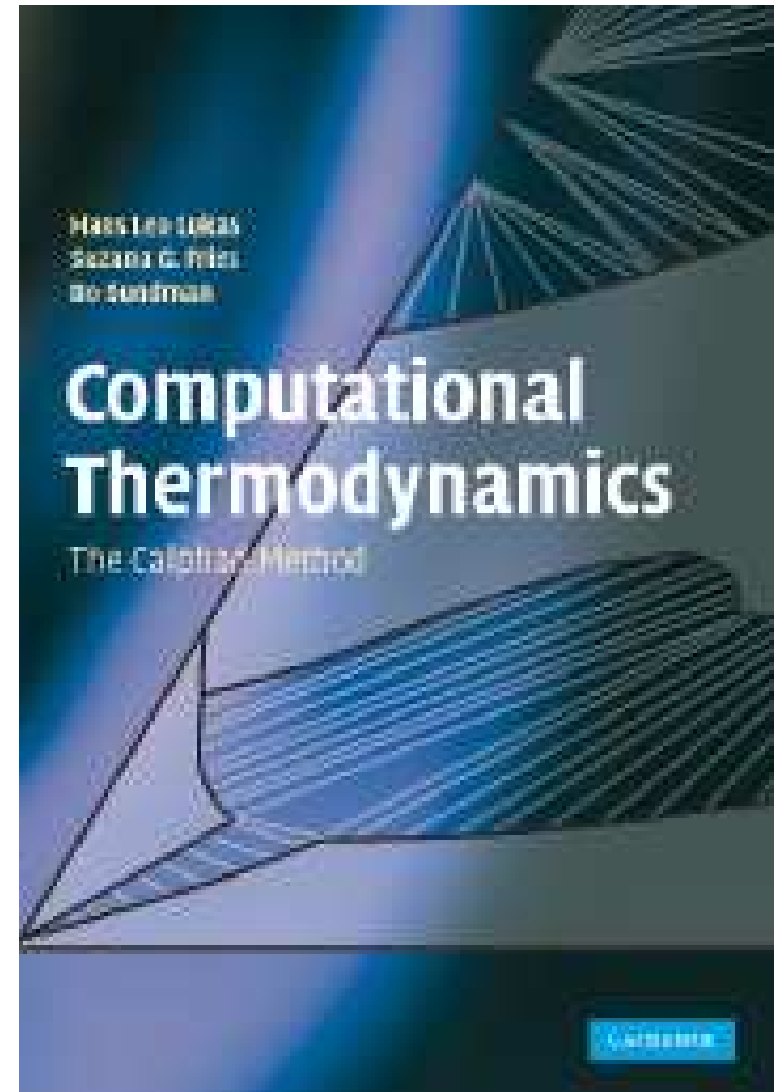


Metastable fcc ordering in Al-Fe

There is also a small region of fcc in the Al-Fe and by adding C this expands significantly and there is also an ordered carbide with the perovskite structure, Fe_3AlC . In order to model this correctly one must assess the metastable ordering of the fcc phase in the binary Al-Fe system using ab initio calculations. The carbide could then be modeled similar to an ordered fcc phase. Calphad **32**, (2008) 361-370

Read more

- Learn more about using models and how to do assessments
- Also recommended:
- Hillert: Phase equilibria, phase diagrams and phase transformations
- Saunders and Miodownik: Calphad



Summary

- Many important quantities needed for simulations of phase transformation are provided by thermodynamics.
- But this requires that the extrapolations of the assessed thermodynamic properties outside the stable ranges of the phases are reasonable.
- And this requires extra efforts in the assessment of thermodynamic data and phase diagrams making use of ab initio calculations for the metastable states for example.
- Many systems assessed 10-20 years ago need reassessments, starting with the pure elements, as the extrapolations are not very reliable.
- Systematic assessments of thermophysical data (volume-pressure) and kinetic data should be started.
- Software for simulations of phase transformations (phase field methods) should be based on consistent and assessed thermodynamic data..

END