Assessment Fundamentals

Bo Sundman

INSTN, CEA Saclay

Email: Bo.Sundman@cea.fr

Content

- Classical and Materials Thermodynamics

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures
- Thermodynamics and First Principles

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures
- Thermodynamics and First Principles
- Thermodynamic Models of Phases, also in Metastable ranges

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures
- Thermodynamics and First Principles
- Thermodynamic Models of Phases, also in Metastable ranges
- Assessment of Model Parameters
    - All kinds of experimental data can be used, enthalpies, heat capacities, activities, phase diagrams, solubilities, invariants, defects, volumes.
    - Theoretical results from first principles calculations are used.
    - Databases with binary and ternary assessments allows accurate extrapolations to multicomponent systems.

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures
- Thermodynamics and First Principles
- Thermodynamic Models of Phases, also in Metastable ranges
- Assessment of Model Parameters
  - All kinds of experimental data can be used, enthalpies, heat capacities, activities, phase diagrams, solubilities, invariants, defects, volumes.
  - Theoretical results from first principles calculations are used.
  - Databases with binary and ternary assessments allows accurate extrapolations to multicomponent systems.
- Simulation of Phase Transformation: Driving Forces and Gradients of Chemical Potentials

Content

- Classical and Materials Thermodynamics
- Thermodynamics and Microstructures
- Thermodynamics and First Principles
- Thermodynamic Models of Phases, also in Metastable ranges
- Assessment of Model Parameters
  - All kinds of experimental data can be used, enthalpies, heat capacities, activities, phase diagrams, solubilities, invariants, defects, volumes.
  - Theoretical results from first principles calculations are used.
  - Databases with binary and ternary assessments allows accurate extrapolations to multicomponent systems.
- Simulation of Phase Transformation: Driving Forces and Gradients of Chemical Potentials
- Concluding remarks

Thermodynamics, classical

Thermodynamics was originally derived as a phenomenological relation between “work” and “heat”. It is based on two very simple “laws” that are valid for systems in the macroscopic world

- Energy cannot be created or destroyed.
- Heat will never flow spontaneously from a cold to a hot body.

In the nuclear world we know mass can be converted to energy and vice versa but the first law is valid in all practical materials applications.

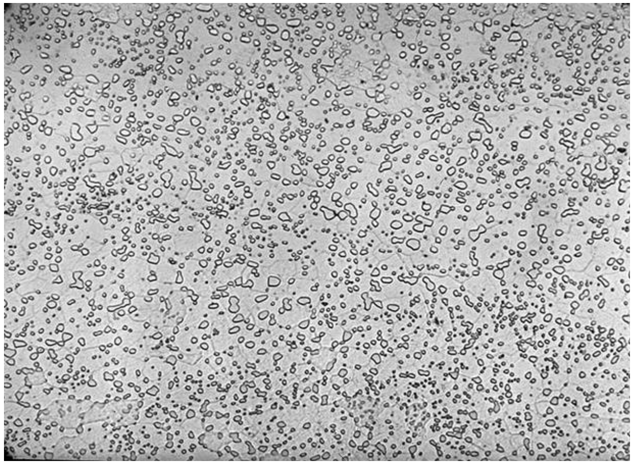
The second law defines the equilibrium state and have the interesting philosophical consequence that it specifies a direction of time. In a world where time goes backward we would violate the second law.

The first law is used to define the *internal energy*, denoted U, and the second law to define the *entropy*, denoted S. These are called “state variables” because they depend only on the state of the system, not how that state was reached.

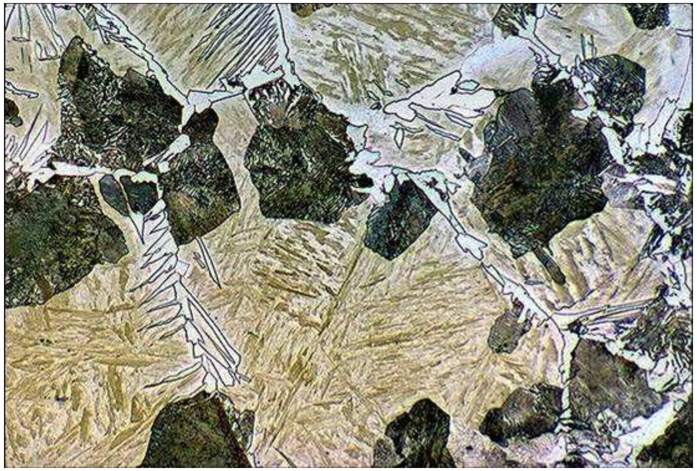
Thermodynamics for materials

The thermodynamics used for materials has nothing to do with “heat” and “work”, it is simply as a tool to determine the stable set of phases in the system, their composition and how state variables depend on temperature, pressure and composition.

The particular problem we have to deal with in material science is that most phases have a significant composition range and we often have materials far from the equilibrium state, for example quenched from a high temperature.



a) Soft annealed steel

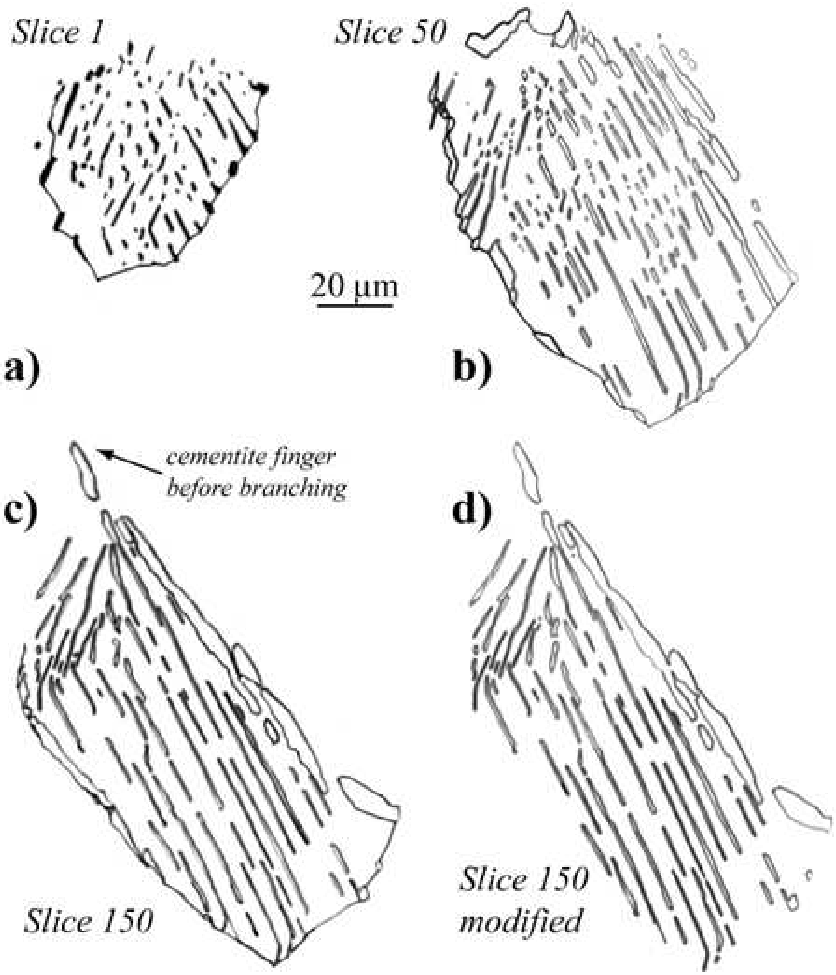


b) Hardened steel

Two different microstructures of the same steel are shown above. The amount, composition and spatial arrangement of the different phases determine the properties. Thermodynamic models have played a key role to understand and control these processes.

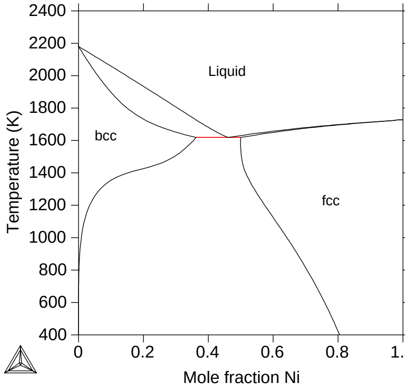
Pearlite movie

Mats Hillert and Nils Lange studied the growth of a pearlite nodule by taking pictures of layer by layer of polished surfaces. This has later been made into a movie which illustrates the growth of the nodule, so **MOVIE TIME**

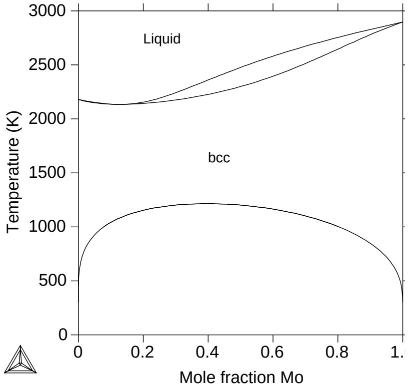


Thermodynamics, composition dependence

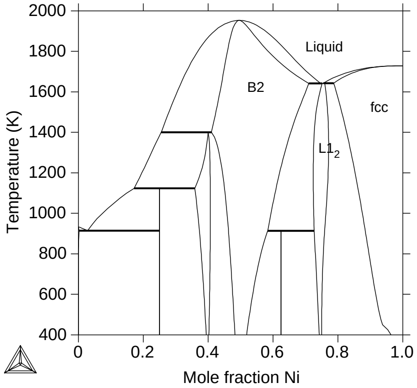
The Calphad technique is specially designed to deal with **extensive solubilities** of the phases in **multi-component systems**. Many of the phases have strong deviation from ideallity, either forming miscibility gaps or ordered compounds. This requires careful modelling of the constitution of each phase.



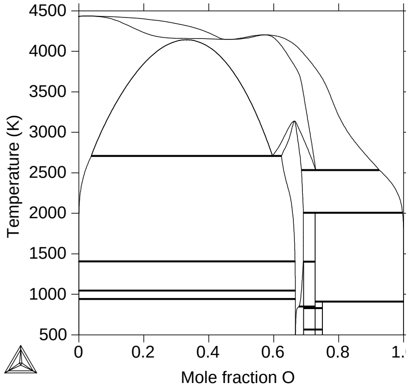
a) Cr-Ni



b) Cr-Mo



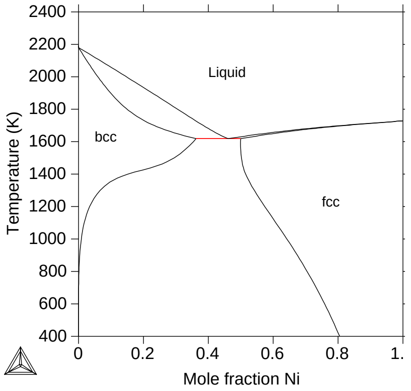
c) Al-Ni



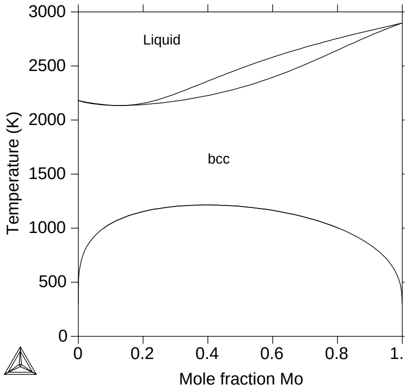
d) U-O

Thermodynamics, composition dependence

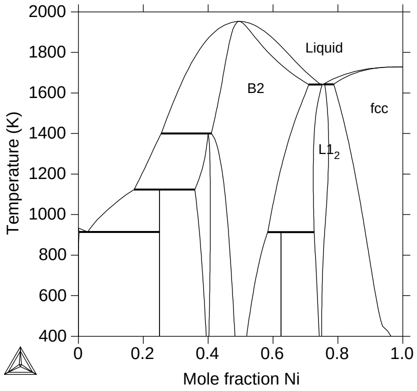
The Calphad technique is specially designed to deal with **extensive solubilities** of the phases in **multi-component systems**. Many of the phases have strong deviation from ideallity, either forming miscibility gaps or ordered compounds. This requires careful modelling of the constitution of each phase.



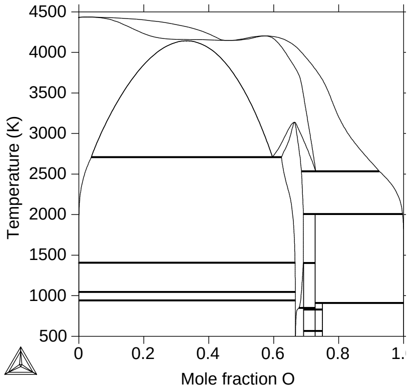
a) Cr-Ni



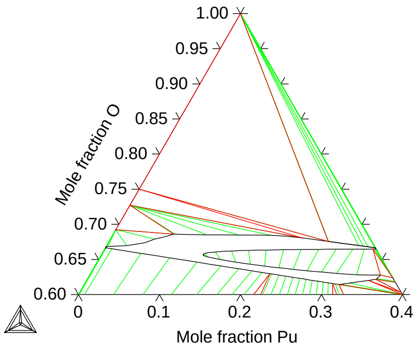
b) Cr-Mo



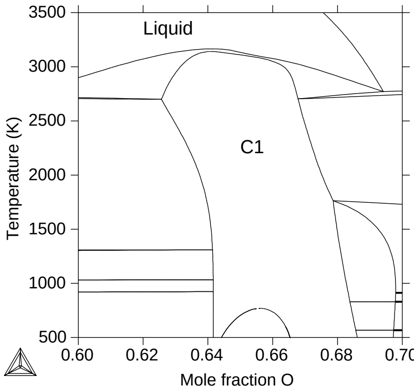
c) Al-Ni



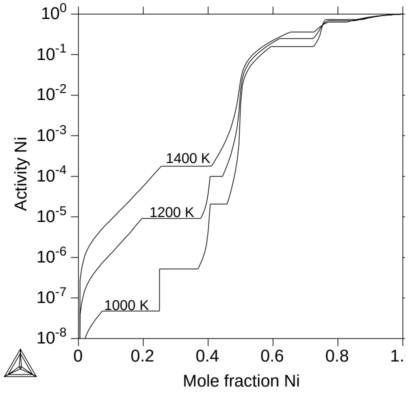
d) U-O



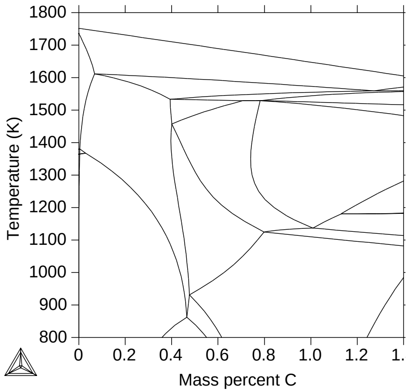
e) O-Pu-U, T=700 K



f) O-Pu-U, $x_{\mathrm{Pu}} = 0.15$



g) Al-Ni, a_{Ni}



h) HSS

Thermodynamics, composition dependence

We cannot use an *Equation of States* (EOS) for the modelling as such equations have no unique way to describe the composition dependence, an EOS is suitable only for systems where the phases have fixed compositions.

The function used in Calphad for modelling is the Gibbs energy, G, because it will be at a minimum at equilibrium at constant composition, T and P, i.e. the most common experimental conditions.

$$dG = -SdT + VdP + \sum_i \mu_i dN_i \tag{1}$$

where μ_i and N_i are the chemical potential and moles of component i respectivly.

Thermodynamics becomes much simpler when we have selected a single dependent function. We can let the computer software make the appropriate transformations to calculate the interesting properties for any kind of conditions.

Thermodynamics, configurational entropy

When a phase can vary in composition the most important contribution to the model is the configurational entropy. Boltzmann derived a relation between entropy and the number of possible configurations of a system, Ω

$$S = k\ln(\Omega) \tag{2}$$

where k is now known as Boltzmann's constant. For a simple case with several kinds of constituents which are distributed randomly on a given number of sites in the phase this relation can be written

$$S_m = R\sum_i x_i\ln(x_i) \tag{3}$$

where $R = N_A k$, (N_A is Avogadro's number) and x_i is the mole fraction of each kind of constituent. The subscript m on the entropy indicates it is per mole. In an ideal solution the chemical potential μ_i of a component i at temperature T is

$$\mu_i = RT\ln(x_i) \tag{4}$$

and its activity equal to the mole fraction.

Calphad history, composition models

The calculation of thermodynamic equilibrium using thermodynamic models requires solving systems of non-linear equations which is practically impossible without a computer.

When Calphad started 40 years ago the computers were very slow and the thermodynamic models were very simple. The assessment technique to determine the model parameters in the Gibbs energy expressions was also primitive.

But from the beginning all kinds of data that can be derived from the Gibbs energy was used: **thermochemical data** like enthalpies of formation, transformation and mixing, heat capacities, chemical potentials and activities and also experimental **phase diagram data** like solubilities, compositions and temperatures at invariant equilibria etc.

Calphad history, composition models

The calculation of thermodynamic equilibrium using thermodynamic models requires solving systems of non-linear equations which is practically impossible without a computer.

When Calphad started 40 years ago the computers were very slow and the thermodynamic models were very simple. The assessment technique to determine the model parameters in the Gibbs energy expressions was also primitive.

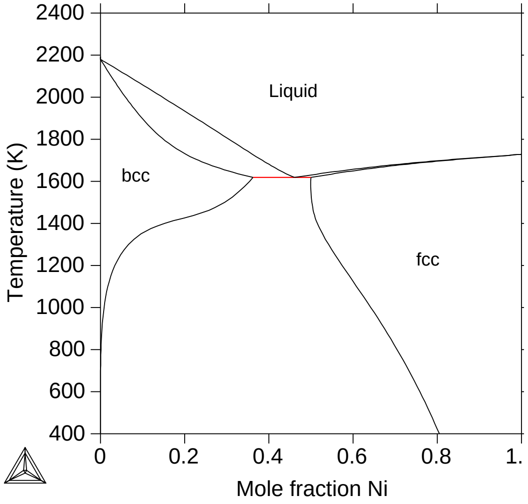
But from the beginning all kinds of data that can be derived from the Gibbs energy was used: **thermochemical data** like enthalpies of formation, transformation and mixing, heat capacities, chemical potentials and activities and also experimental **phase diagram data** like solubilities, compositions and temperatures at invariant equilibria etc.

The models have gradually improved taking more physical properties into account like stoichiometric constraints, magnetism, chemical ordering, composition dependent volumes, etc. The software has also improved so we can calculate systems with 10-12 components and incorporate first principles data in the assessments.

Calphad history, temperature extrapolation

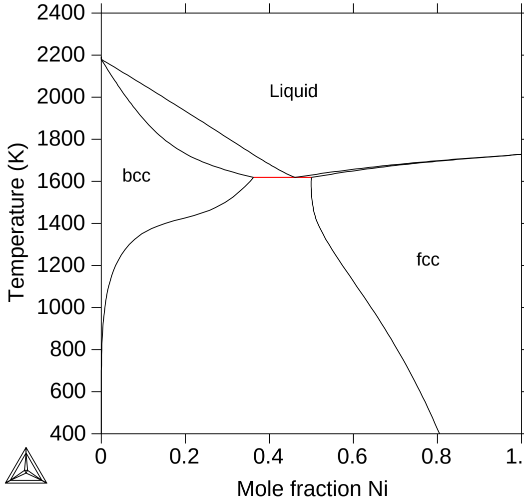
The melting temperature changes when mixing two or more elements as shown in this phase diagram for Cr-Ni. In order to model a liquid mixture at lower temperature than the melting temperature of the elements one must extrapolate the Gibbs energy of the liquid below the melting temperature.

This can be made most simply by using the facts that the Gibbs energy for the liquid and solid is equal at the melting temperature and that $G = H - TS$.



Calphad history, temperature extrapolation

The melting temperature changes when mixing two or more elements as shown in this phase diagram for Cr-Ni. In order to model a liquid mixture at lower temperature than the melting temperature of the elements one must extrapolate the Gibbs energy of the liquid below the melting temperature.



This can be made most simply by using the facts that the Gibbs energy for the liquid and solid is equal at the melting temperature and that $G = H - TS$.

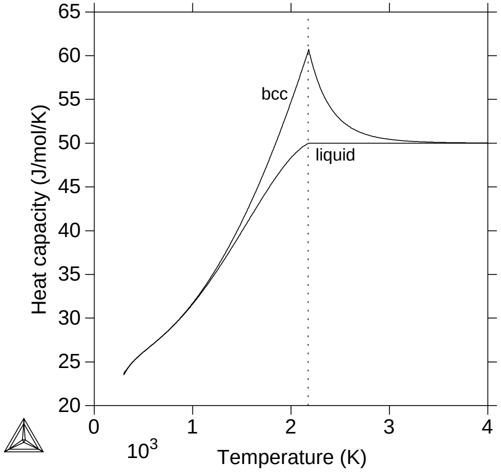
We introduce the enthalpy of fusion as the difference between the enthalpies of liquid and bcc at the melting temperature, $T_f\,:\;\Delta H_f = H^{\rm liquid} - H^{\rm bcc}$ and assuming ΔH_f is constant the Gibbs energy for the liquid relative to the solid is:

$$G^{\rm liquid}_{\rm Cr} = G^{\rm bcc}_{\rm Cr} + \Delta H_f(1 - \frac{T}{T_f}) \tag{6}$$

But this extrapolation of G is not realistic because the heat capacities of the liquid and solid are different, also at the melting temperature.

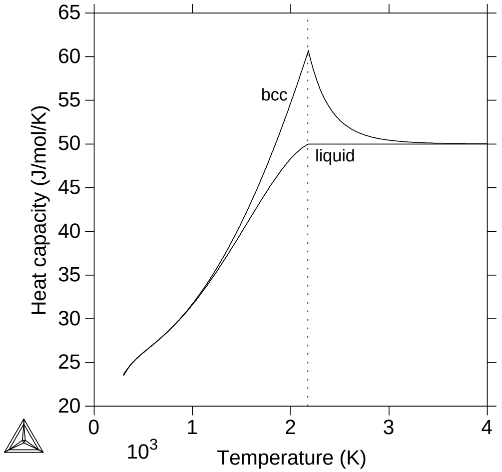
Calphad history, Temperature extrapolation

As it is thermodynamically impossible to have a jump in the heat capacity in a single phase region SGTE introduced an extrapolation that makes the heat capacity continuous as shown in the figure. It makes the liquid heat capacity approach that of bcc below the melting temperature and vice versa.

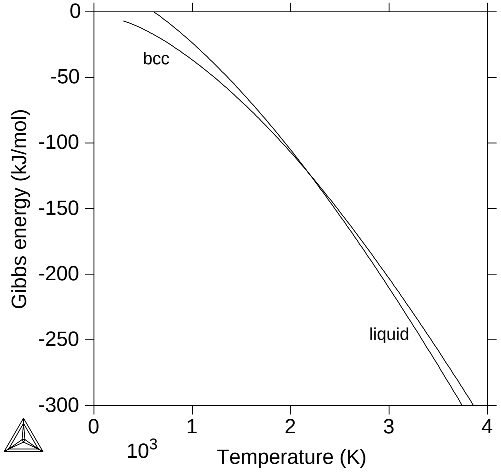


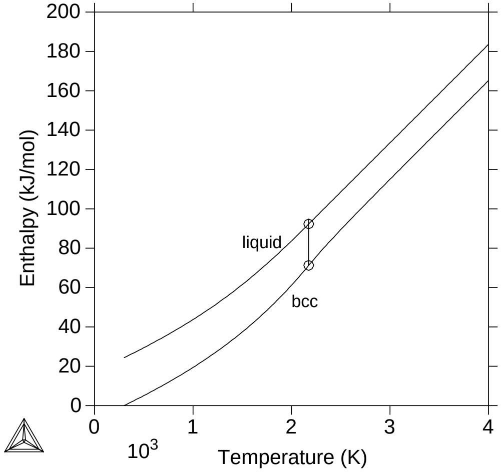
Calphad history, Temperature extrapolation

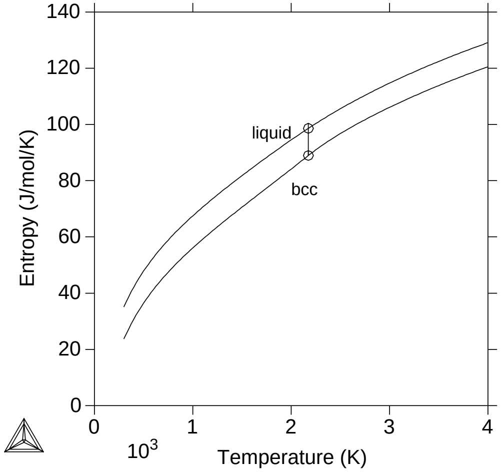
As it is thermodynamically impossible to have a jump in the heat capacity in a single phase region SGTE introduced an extrapolation that makes the heat capacity continuous as shown in the figure. It makes the liquid heat capacity approach that of bcc below the melting temperature and vice versa.



These figures show how G, H and S are extraplolated from 300 to 4000 K for the liquid and bcc for pure Cr using the SGTE method. The enthalpy and entropy of melting are marked.







Calphad history, Metastable states

In the Calphad technique each crystalline phase is also modelled separately and the **modelled Gibbs energy function** for a solution phase will normally extend between all pure element in a system.

But many phases dissolve elements which are never stable for the element as pure. So make it possible to extrapolate the Gibbs energy of a solution phase to the pure elements we must introduce so called **lattice stabilities**. These describe the difference in Gibbs energy between the solution phase and the stable phase for the pure element.

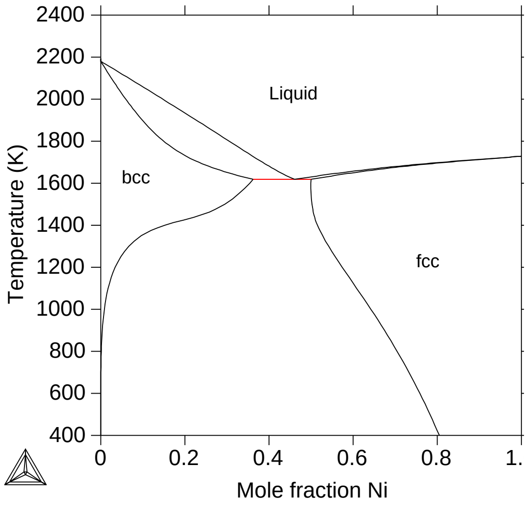
Calphad history, Metastable states

In the Calphad technique each crystalline phase is also modelled separately and the **modelled Gibbs energy function** for a solution phase will normally extend between all pure element in a system.

But many phases dissolve elements which are never stable for the element as pure. So make it possible to extrapolate the Gibbs energy of a solution phase to the pure elements we must introduce so called **lattice stabilities**. These describe the difference in Gibbs energy between the solution phase and the stable phase for the pure element.

We have seen that the Gibbs energy function of the liquid phase for a pure element below the melting point can be extrapolated using ΔH_f and making the heat capacities approach each other.

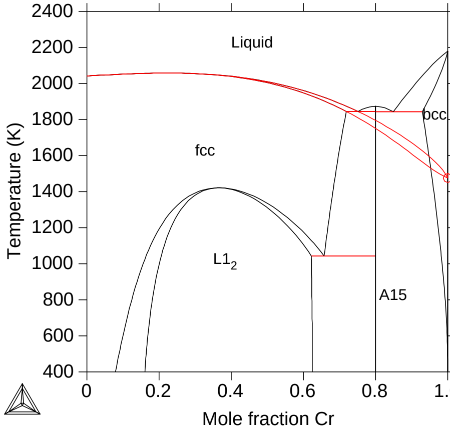
But how to handle crystalline phases that are never stable for the element as pure? In the phase diagram for the Cr-Ni system there is considerable solibility of Cr in fcc and Ni in bcc. But pure Cr is never stable with an fcc lattice and pure Ni never stable with a bcc lattice.



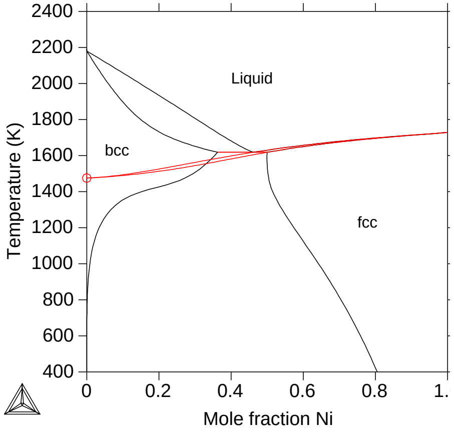
Calphad history, lattice stabilities

The first set of lattice stabilities was proposed by Larry Kaufman more than 40 years ago. One of the estimation techniques he used is illustrated below for fcc-Cr.

The liquidus for several binaries with high solubility of Cr in fcc can be extrapolated to a metastable melting temperature for fcc-Cr. Combined with an estimated melting entropy this gives the difference in Gibbs energy between fcc and bcc Cr.



a) Pt-Cr



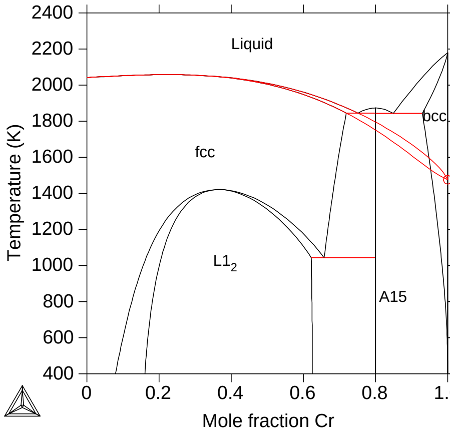
b) Cr-Ni

The liquidus and solidus curves for fcc/liquid has been extrapolated to pure Cr to estimate a metastable melting point. It must be the same independent of the alloying element.

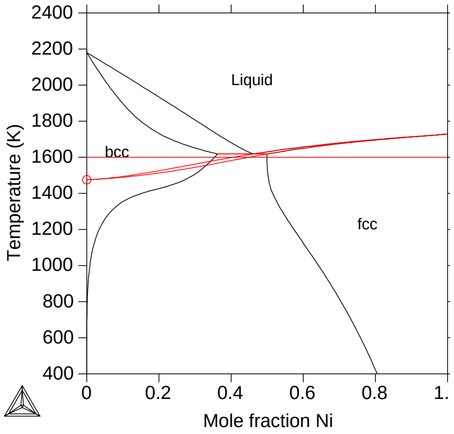
Calphad history, lattice stabilities

The first set of lattice stabilities was proposed by Larry Kaufman more than 40 years ago. One of the estimation techniques he used is illustrated below for fcc-Cr.

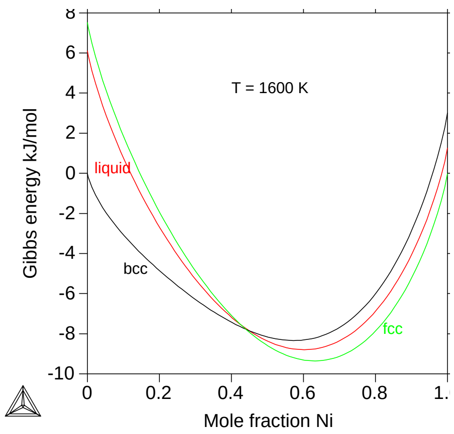
The liquidus for several binaries with high solubility of Cr in fcc can be extrapolated to a metastable melting temperature for fcc-Cr. Combined with an estimated melting entropy this gives the difference in Gibbs energy between fcc and bcc Cr.



a) Pt-Cr



b) Cr-Ni



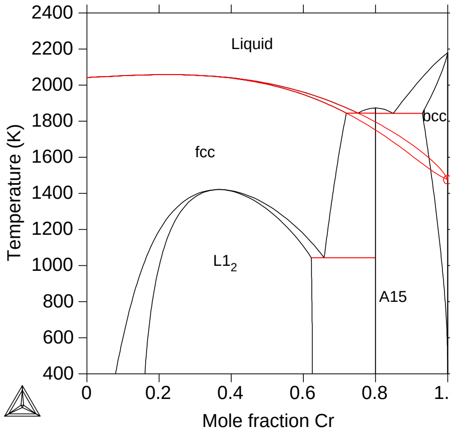
c) Cr-Ni

The right hand figure shows how the Gibbs energy for the different phases in Cr-Ni vary with composition at 1600 K. The end point of the fcc curve for pure Cr is the “lattice stability” of fcc-Cr at 1600 K, slightly above the liquid.

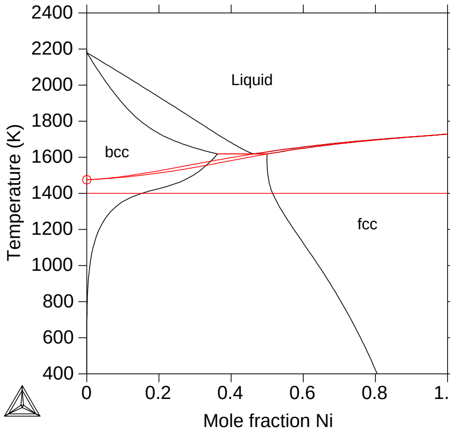
Calphad history, lattice stabilities

The first set of lattice stabilities was proposed by Larry Kaufman more than 40 years ago. One of the estimation techniques he used is illustrated below for fcc-Cr.

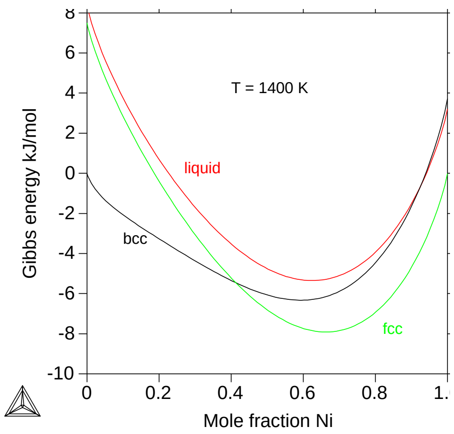
The liquidus for several binaries with high solubility of Cr in fcc can be extrapolated to a metastable melting temperature for fcc-Cr. Combined with an estimated melting entropy this gives the difference in Gibbs energy between fcc and bcc Cr.



a) Pt-Cr



b) Cr-Ni

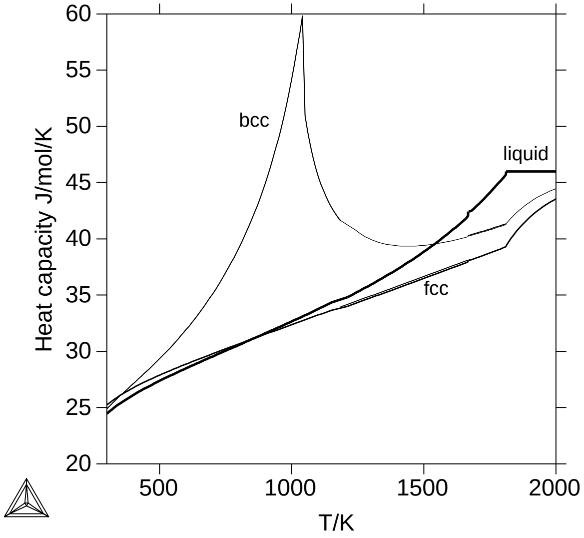


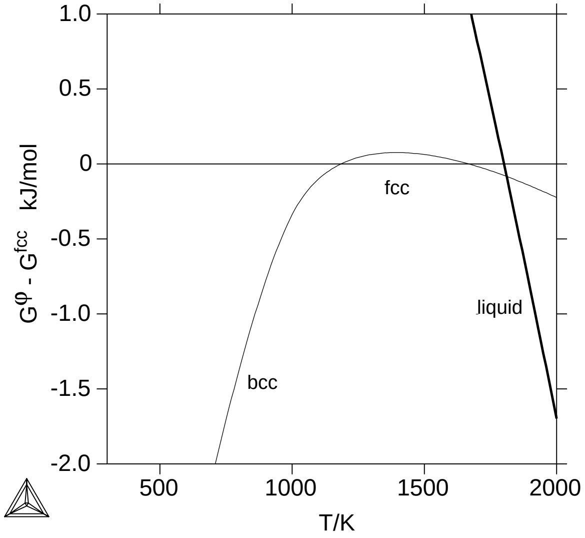
d) Cr-Ni

The right hand figure is now the Gibbs energy curves at 1400 K, now the lattice stability for fcc-Cr is below that of the liquid. Today lattice stabilities can be calculated by first principles but such data are sometimes not useful because the metastable states of the pure elements are often mechanically unstable.

Pure Fe

For a more complicated case like pure Fe the heat capacity extrapolations and the Gibbs energy differences relative to fcc is shown in the figures below. The magnetic transition in bcc has a significant influence on the thermodynamic properties.





The heat capacities of crystalline phases that are never stable for an element are usually set equal to the Stable Element Reference (SER) i.e. the stable phase at 298.15 K and 1 bar (also in temperature regions where this is metastable). For elements with many stable phases, like Pu, these phases may become more or less metastable in different temperature ranges.

Thermodynamic models must be based on integral functions

An early conflict between calphadists and chemists was models based on activity coefficients. A simple way to extend the use of chemical reactions to non-ideal solution phases is to use an activity coefficient, γ_i

$$\mu_i = RT\ln(\gamma_i x_i) \tag{7}$$

When γ_i is constant we have the so called “Henry’s model” which is still popular for dilute solutions. But if we try to extend this model by making γ_i composition dependent we must not forget that the integral Gibbs energy, for N moles of components, is

$$G = N\sum_i x_i\mu_i \tag{8}$$

and that the definition of the chemical potentials is

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} \tag{9}$$

where $N_i = Nx_i$.

Only a very limited set of composition dependencies of the chemical potentials (or activity coefficients) does not violate these relations. And they must always be derived from an integral Gibbs energy function.

Thermodynamic models, the modelling function

In the Calphad community we have a long experience of developing composition models of condenced phases and we all agree is that the thermodynamic properties for a system with several composition dependent phase must be calculated from the total Gibbs energy modelled as

$$G(T, P, x_i) = \sum_{\alpha} N^{\alpha} G_m^{\alpha}(T, P, x_i^{\alpha}) \tag{10}$$

where α is the phase, N^{α} the amount of the phase and G_m^{α} the molar Gibbs energy of the phase. x_i^{α} is the fraction of component i in the α phase.

The expression for G_m^{α} is still an intensive field of scientific development and we try to include as much as possible of the physical properties of the phase like crystal structure, magnetism, ordering, charge transfer etc. still keeping in mind that the model must be possible to use for multicomponent systems.

Thermodynamic models, the Compound Energy Formalism

For crystalline phases we may have different types of sites that is occupied by different constituents. The most general way to describe such phases is the Compound Energy Formalism (CEF). This can handle any number of sublattices, any kind of constituents (atoms, vacancies, ions, molecules) on the sublattices and different kinds of interactions between these constituents. Its generic expression is

$$G_m = {}^{\mathrm{srf}}G_m - T\,{}^{\mathrm{cfg}}S_m + {}^{E}G_m + {}^{\mathrm{phys}}G_m \tag{11}$$

where ${}^{\mathrm{srf}}G_m$ is the surface of reference including lattice stabilites, ${}^{\mathrm{cfg}}S_m$ is the configurational entropy assuming ideal mixing of the constituents on each sublattice, ${}^{E}G_m$ is the “excess” Gibbs energy describing interaction energies of the constituents and ${}^{\mathrm{phys}}G_m$ describe particular physical properties like magnetic transitions.

${}^{\mathrm{srf}}G_m$ and ${}^{E}G_m$ contain model parameters that must be fitted to experimental and theoretical data in an assessment procedure.

Thermodynamic models, the Compound Energy Formalism

The terms in the Gibbs energy can in the general case be expressed as

$$ {}^{\mathrm{srf}}G_m = \sum_I \Pi_I(Y)\,{}^{\circ}G_I(T) \tag{12} $$

where I is an array specifying one constituent in each sublattice and $\Pi_I(Y)$ is the product of their constituent fractions. Thus I specifies a “compound” or *end member* and ${}^{\circ}G_I(T)$ is the energy of formation of this compound. The configurational entropy assumes random mixing in each sublattice and $y_i^{(s)}$ is the fraction of constituent i in sublattice s and a_s is the number of sites in sublattice s

$$ {}^{\mathrm{cfg}}S_m = -R\sum_s a_s \sum_i y_i^{(s)} \ln(y_i^{(s)}) \tag{13} $$

Finally the excess Gibbs energy takes interactions between constituents in the same sublattice into account, where J specifies one or more constituents in each sublattice and $\Pi_J(Y)$ is the product of these fractions and $L_J(T)$ is the interaction energy.

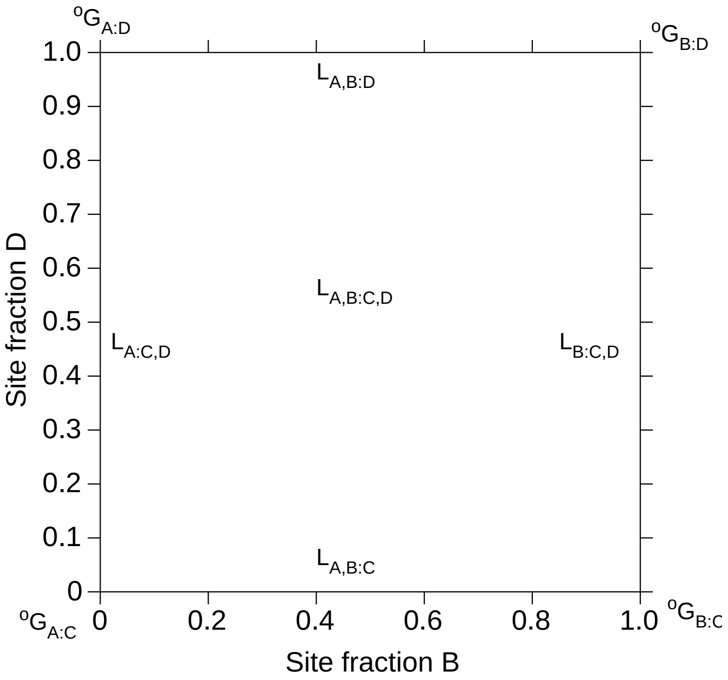
$$ {}^{E}G_m = \sum_J \Pi_J(Y) L_J(T) \tag{14} $$

The ${}^{\mathrm{phys}}G_m$ can be very different for different contributions.

Thermodynamic modelling, the reciprocal system

The simplest case of a sublattice model is the reciprocal system with two sublattices and two constituents in each (A,B)$_a$(C,D)$_c$. There are 4 endmembers and on each side there is an interaction parameter. Additionally there is a special “reciprocal” parameter representing simultaneous interaction with all 4 constituents.

The constituents A, B, C and D can be elements, molecules, ions or vacancies.



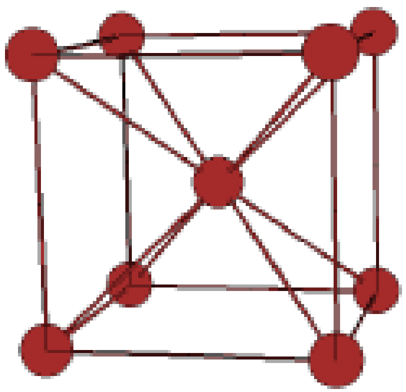
The Gibbs energy expression is

$$G_m = \sum_{i=\mathrm{A,B}} \sum_{j=\mathrm{C,D}} y'_i y''_j \,{}^\circ G_{ij} + RT(a \sum_{i=\mathrm{A,B}} y'_i \ln(y'_i) + c \sum_{j=\mathrm{C,D}} y''_j \ln(y''_j)) + {}^E G_m$$

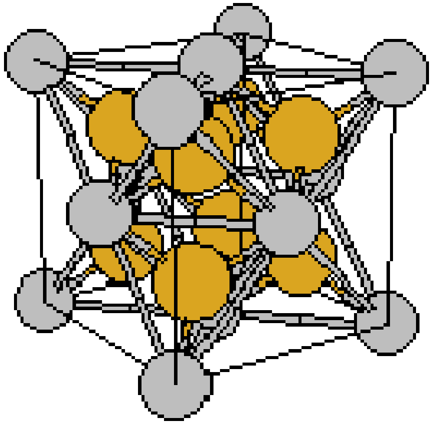
$${}^E G_m = y'_\mathrm{A} y'_\mathrm{B} (y''_\mathrm{C} L_\mathrm{A,B:C} + y''_\mathrm{D} L_\mathrm{A,B:D}) + y''_\mathrm{C} y''_\mathrm{D} (y'_\mathrm{A} L_\mathrm{A:C,D} + y'_\mathrm{B} L_\mathrm{B:C,D}) + y'_\mathrm{A} y'_\mathrm{B} y''_\mathrm{C} y''_\mathrm{D} L_\mathrm{A,B:C,D}$$

Thermodynamic models, the Compound Energy Formalism

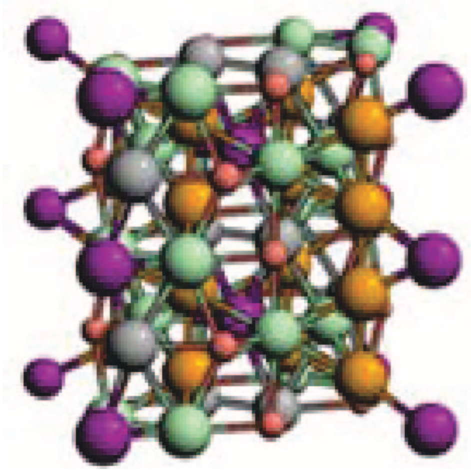
The CEF is a generic formalism that include many simple models like the gas phase with molecules, the substitutional regular solution, stoichiometric compounds with a single constituent on each sublattice, ordered intermetallics like Laves phases, σ phases, carbides, nitrides, ionic compounds like spinel, UO_2 etc.



a) bcc



b) fluorite



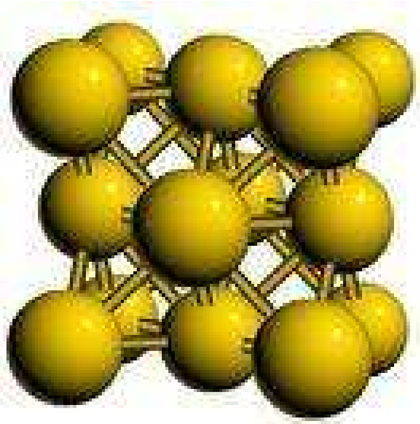
c) σ

For each phase the expressions for ${}^{\mathrm{srf}}G_m$ and ${}^{\mathrm{cfg}}S_m$ etc are different taking the real sublattices and constituents into account.

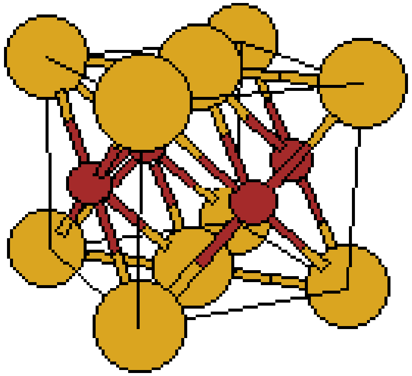
For the magnetic model the ${}^{\mathrm{phys}}G_m$ depend on additional variables like the Curie temperature and the Bohr magneton number which are modelled as functions of the constitution of the phase.

Thermodynamic models, crystalline phases

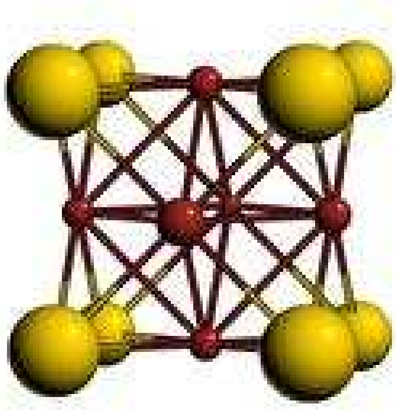
Phases with order/disorder transformations like the fcc structure (that can form $L1_2$ and $L1_0$ ordered structures) or bcc (with B2, B32, $D0_3$ and $L2_1$ ordering) are modelled with 4 sublattices where different fractions of the same constituent on the sublattice can give different Gibbs energies.



a) fcc



b) $L1_0$



c) $L1_2$

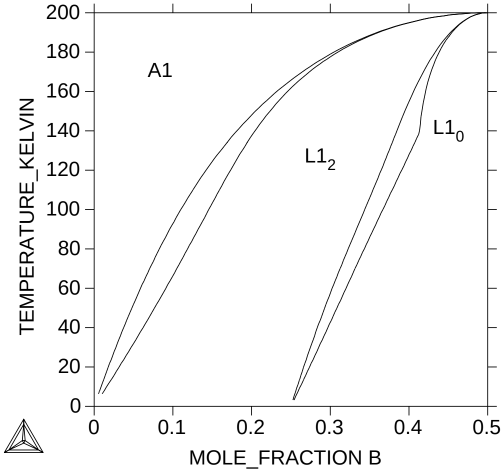
A CEF model for a disordered fcc phase needs a single sublattice (Al,Ni), to model the $L1_2$, $L1_0$ and fcc we need four sublattices representing the symmetrical tetrahedron:

$(\mathrm{Al}, \mathrm{Ni})_{0.25}(\mathrm{Al}, \mathrm{Ni})_{0.25}(\mathrm{Al}, \mathrm{Ni})_{0.25}(\mathrm{Al}, \mathrm{Ni})_{0.25}$

The sublattices describe the long range order (LRO) and the contribution to the Gibbs energy due to short range order (SRO) can be included as an excess energy.

FCC ordering with Bragg-Williams, CVM and CEF

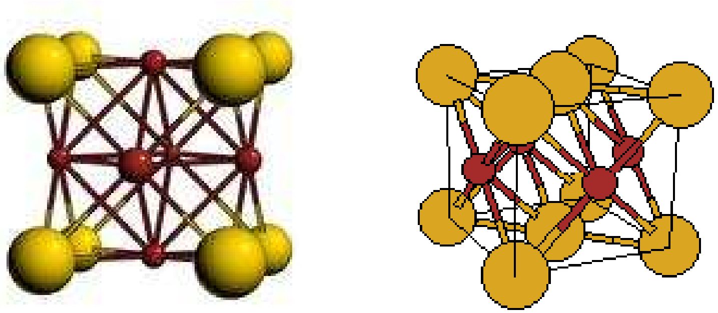
The classical Shockley diagram using Bragg-Williams approximation for fcc ordering. This has wrong topology as the $L1_2$ and $L1_0$ disorder at the same temperature and composition and as second order. It uses a single A-B bond energy and random (point) approximation of the configurational entropy.



There are 16 endmembers in the Gibbs energy for the Bragg-Williams model with 4 sublattices: $(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}(A,B)_{0.25}$

$$G_m^{\mathrm{BW}} = \sum_i \sum_j \sum_k \sum_l y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} \; {}^\circ G_{ijkl} + RT \sum_s 0.25 \sum_i y_i^{(s)} \ln(y_i^{(s)})$$

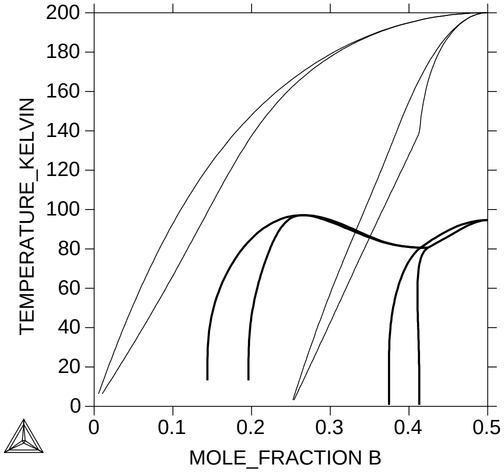
$$\begin{aligned} {}^\circ G_{\mathrm{AAAA}} &= 0 \\ {}^\circ G_{\mathrm{AAAB}} &= 4u_{\mathrm{AB}} \\ {}^\circ G_{\mathrm{AABB}} &= 6u_{\mathrm{AB}} \end{aligned}$$



FCC ordering with Bragg-Williams, CVM and CEF

Here the Shockley diagram is overlayed with a CVM calculation using the tetrahedron approximation of the configurational entropy. The same A-B bond energy is used for both diagrams.

For the CVM the ordering has now separate maxima for the $L1_2$ and $L1_0$ ordering as it should be. The ordering temperature is also half that of the Shockley diagram.



$$
\begin{aligned}
G_m^{\mathrm{CVM}} &= \sum_i \sum_j \sum_k \sum_l \sigma_{ijkl}\, {}^\circ G_{ijkl} + \\
&\quad RT\left(2\sum_{ijkl} \sigma_{ijkl}\ln(\sigma_{ijkl}) - 6\sum_i\sum_j p_{ij}\ln(p_{ij}) + 5\sum_i y_i\ln(y_i)\right)
\end{aligned}
$$

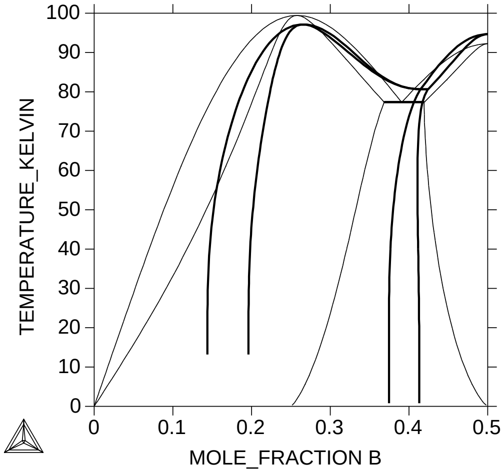
with the same 16 constant “cluster energies” ${}^\circ G_{ijkl}$ as in the Bragg-Williams case. σ_{ijkl} are the tetrahedron cluster probabilities, p_{ij} the pair probabilities and x_i the point probabilities. Replacing $\sigma_{ijkl} = y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)}$ will make this identical to the Bragg-Williams model.

FCC ordering with Bragg-Williams, CVM and CEF

Now the CVM diagram is shown together with a CEF calculation of the same prototype system with the same A-B bond energy. The CEF model uses Bragg-Williams configurational entropy but has added an excess term with a reciprocal parameter with the form

$$^{E}G_m = \sum\sum y'_{\mathrm{A}} y'_{\mathrm{B}} y''_{\mathrm{A}} y''_{\mathrm{B}} u_{\mathrm{AB}}$$

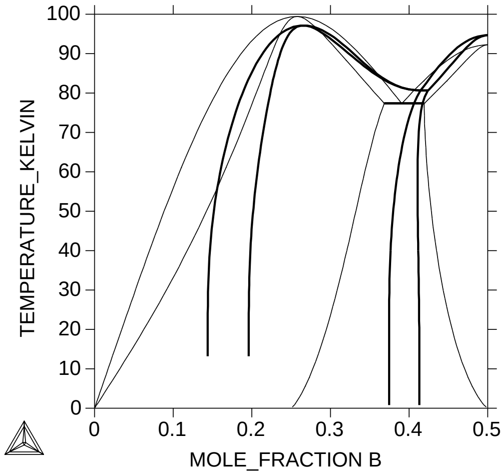
This was first derived in a paper by B Sundman and T Mohri, Z Metallkde., **81** (1990) 251-254.



FCC ordering with Bragg-Williams, CVM and CEF

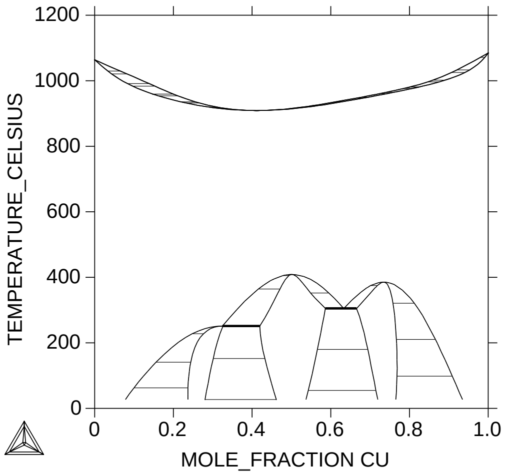
Now the CVM diagram is shown together with a CEF calculation of the same prototype system with the same A-B bond energy. The CEF model uses Bragg-Williams configurational entropy but has added an excess term with a reciprocal parameter with the form

$$^{E}G_m = \sum\sum y'_{\mathrm{A}} y'_{\mathrm{B}} y''_{\mathrm{A}} y''_{\mathrm{B}} u_{\mathrm{AB}}$$



This was first derived in a paper by B Sundman and T Mohri, Z Metallkde., **81** (1990) 251-254.

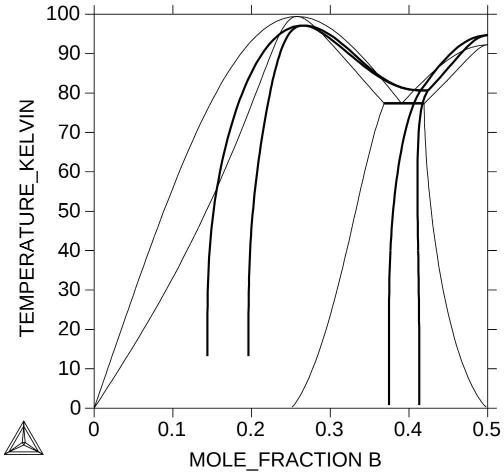
This is an assessment of the Au-Cu phase diagram showing all fcc ordering forms as stable. The CEF model with reciprocal terms are used.



FCC ordering with Bragg-Williams, CVM and CEF

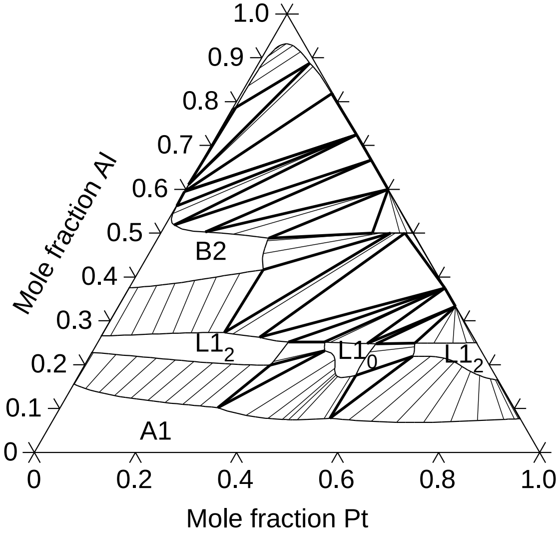
Now the CVM diagram is shown together with a CEF calculation of the same prototype system with the same A-B bond energy. The CEF model uses Bragg-Williams configurational entropy but has added an excess term with a reciprocal parameter with the form

$$^{E}G_m = \sum\sum y'_{\mathrm{A}} y'_{\mathrm{B}} y''_{\mathrm{A}} y''_{\mathrm{B}} u_{\mathrm{AB}}$$



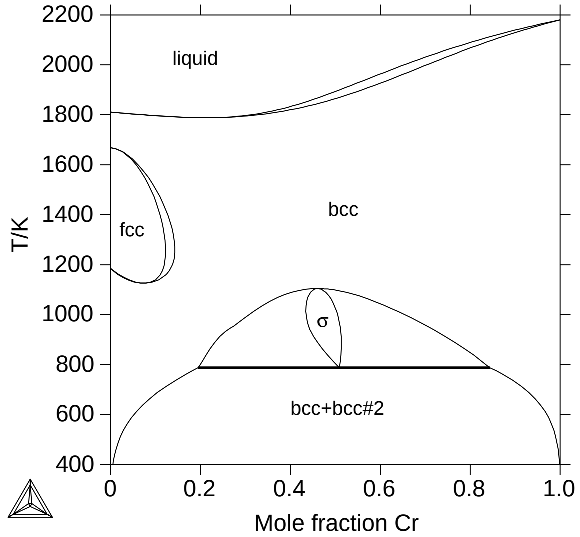
This was first derived in a paper by B Sundman and T Mohri, Z Metallkde., **81** (1990) 251-254.

Here is a ternary extrapolation from the binary assessments of Al-Ni, Al-Pt and Ni-Pt using the CEF model with reciprocal parameters. It shows that extrapolations using this model are not unreasonable. Which is one of the most important Calphad criteria.

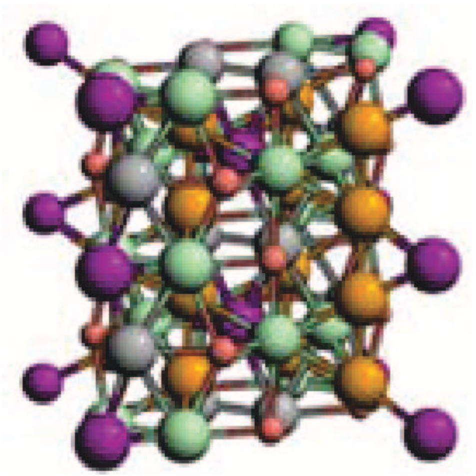


Thermodynamic models, intermetallics

Intermetallic phases have many sublattices, σ has 5, but CEF allows simplifications if there are not sufficient experimental data to model the whole composition range because these phases are usually stable in narrow temperature and composition ranges.



a) The Cr-Fe phase diagram



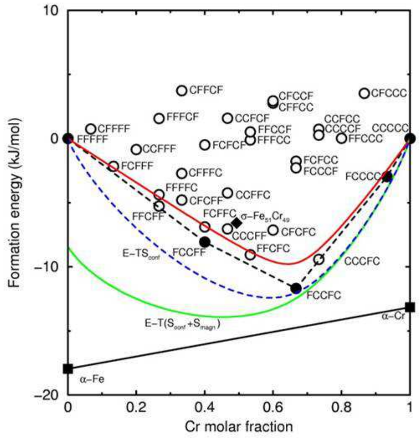
b) The σ structure

Thermodynamic models, intermetallics

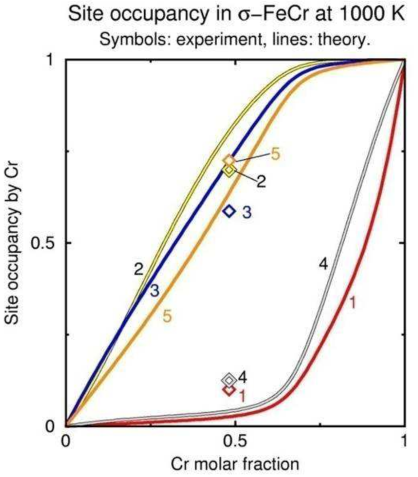
Intermetallic phases have many sublattices, σ has 5, but CEF allows simplifications if there are not sufficient experimental data to model the whole composition range because these phases are usually stable in narrow temperature and composition ranges.

However, with first principles calculations we may calculate all $2^5 = 32$ configurations of a binary σ phase as has been done for Cr-Fe and several other system. The top figure shows the energies for the 32 configurations calculated for Cr-Fe, many have the same composition.

$(Cr,Fe)_2(Cr,Fe)_4(Cr,Fe)_8(Cr,Fe)_8(Cr,Fe)_8$



A 5 sublattice CEF model with the first principles energies inserted as the endmember energies $^\circ G_I$ has been used to calculate the fractions of Cr on the 5 sublattices for varying Cr content at 1000 K in the lower figure. Random configurational entropy on each sublattice is assumed. The symbols represent experimental data in the limited range of stability of the σ phase. In order to fit also the phase diagram and other data the first principles energies must be slightly adjusted.



Thermodynamic models, ionic phases

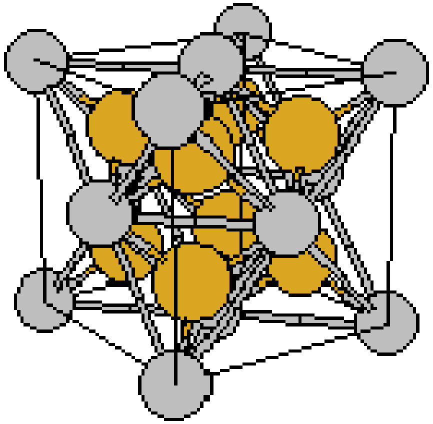
For ionic phases like the spinel we can model the occupancy of the different sublattices by electrically charged elements like in magnetite

$(\mathrm{Fe}^{+2}, \mathrm{Fe}^{+3})_1(\mathrm{Fe}^{+3}, \mathrm{Fe}^{+2}, \mathrm{Va})_2(\mathrm{O}^{-2})_4$

where the ions with different valences are treated as different constituents and Va represent vacant sites on that sublattice. On each sublattice ideal mixing is assumed. For the UO_2 phase with C1 structure the model adopted is

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

where U can take 3 different valences and we have vacancy defects on the oxygen sublattice and an interstitial sublattice for oxygen.



Thermodynamic models, ionic phases

For ionic phases like the spinel we can model the occupancy of the different sublattices by electrically charged elements like in magnetite

$(\mathrm{Fe}^{+2}, \mathrm{Fe}^{+3})_1(\mathrm{Fe}^{+3}, \mathrm{Fe}^{+2}, \mathrm{Va})_2(\mathrm{O}^{-2})_4$

where the ions with different valences are treated as different constituents and Va represent vacant sites on that sublattice. On each sublattice ideal mixing is assumed. For the UO_2 phase with C1 structure the model adopted is

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

where U can take 3 different valences and we have vacancy defects on the oxygen sublattice and an interstitial sublattice for oxygen.

This model describes the LRO of the phase. To model also the SRO many clusters must be used and the configurational entropy must be derived using CVM. The great advantage with CEF is that it is easy to extend the model adding more constituents:

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

A Wagner-Schottky model may be simpler to use in a binary system but such a model does not have this flexibility to multi-component extrapolations.

Thermodynamic models, liquids

The liquid phase is one of the most complex to model as it can vary its properties significantly with composition like metallic, covalent, ionic etc. In some cases different models are used for the liquid at different composition ranges in the same system but that is not scientifically satisfactory.

The most flexible model available is the partially ionic two-sublattice model which can describe all kinds of liquids (except aqueous) but which requires accurate experimental data for the liquid which are often missing.

First principle data is normally not available for liquids but we may select models and constituents based on results both from experiments and molecular dynamics simulations. For ionic liquids the cations and anions are assumed to mix idependently and the model for U-Pu-O is

$$(\mathrm{Pu}^{+3}, \mathrm{U}^{+4})_P(\mathrm{O}^{-2}, \mathrm{Va}, \mathrm{PuO}_2, \mathrm{O})_Q$$

where the “site ratios” P and Q vary with the constitution to make the liquid electrically neutral. The vacancy in the anion sublattice is needed to describe the metallic liquid without anions and the neutral constituent O describes the metatstable liquid oxygen.

Calculating the equilibrium

With a model for each phase in a system we need a software to calculate the equilibrium of the system by minimizing the Gibbs energy for different conditions. The most general method for finding the equilibrium is a total Gibbs energy minimisation with constraints. This can easily take into account different models for the different phases and also change the set of stable phases while iterating.

The simplest set of conditions is fixed T, P and overall composition. One or more of these conditions can be replaced by a condition on the activity or chemical potential of a component.

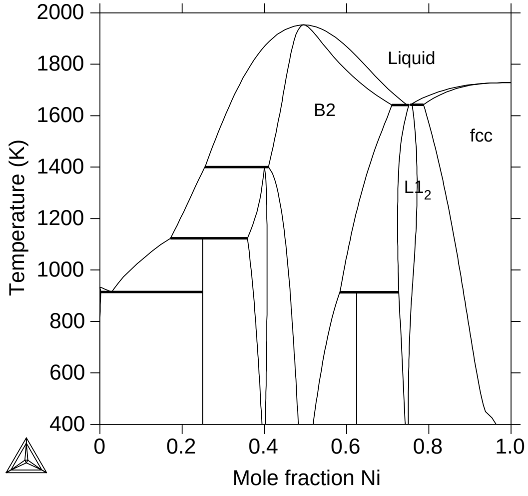
It is also possible to have as condition that one or more phases, like the liquid, must be stable. We may even specify the composition of a phase constituent as a condition and in some cases we may be interested to calculate an equilibrium with the condition that the enthalpy of the system should have a given value.

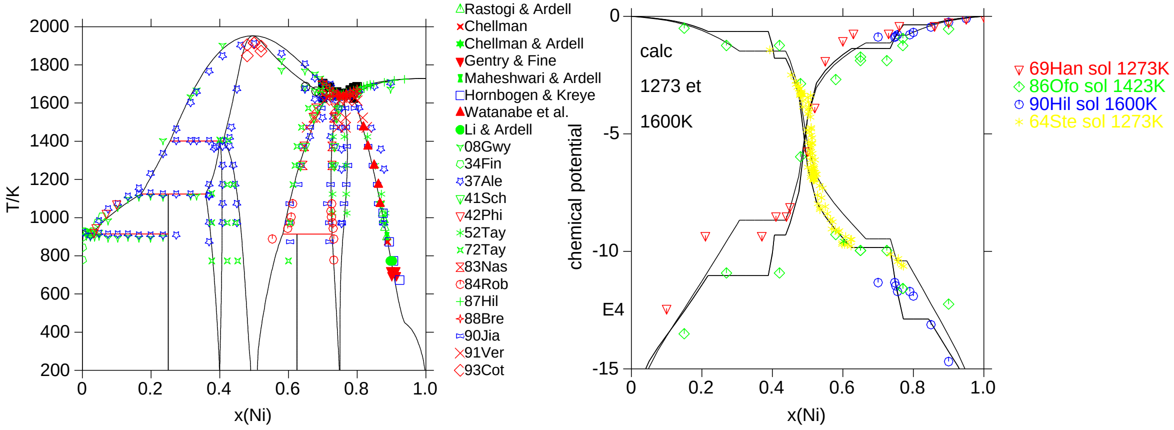
But the number of conditions is limited by the Gibbs phase rule, $f = n - p + 2$.

How G, μ and phase diagram are connected

The powerful feature of Calphad is the ability to model the composition dependence and we will investigate how the thermodynamic properties vary with the composition, derived from the Gibbs energy for each phase.

The Al-Ni phase diagram to the right has been calculated from an assessment of all phases stable in this system. The phase diagram and chemical potentials are also shown together with experimental data below.



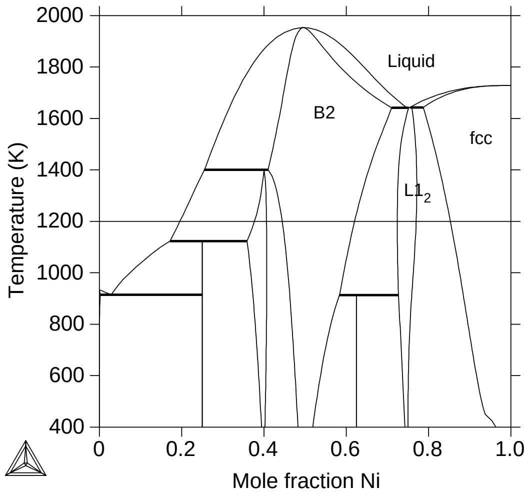


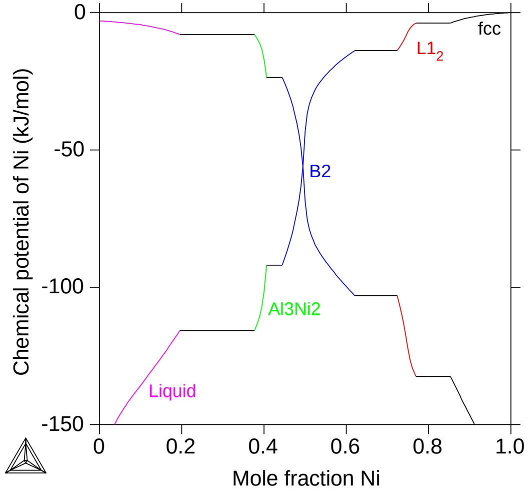
How G, μ and phase diagram are connected

As all thermodynamic properties can be calculated from the assessed Gibbs energies we can also calculate the chemical potentials as shown in the lower figure for both Al and Ni at 1200 K. The reference state for the chemical potential has been selected as fcc for both elements.

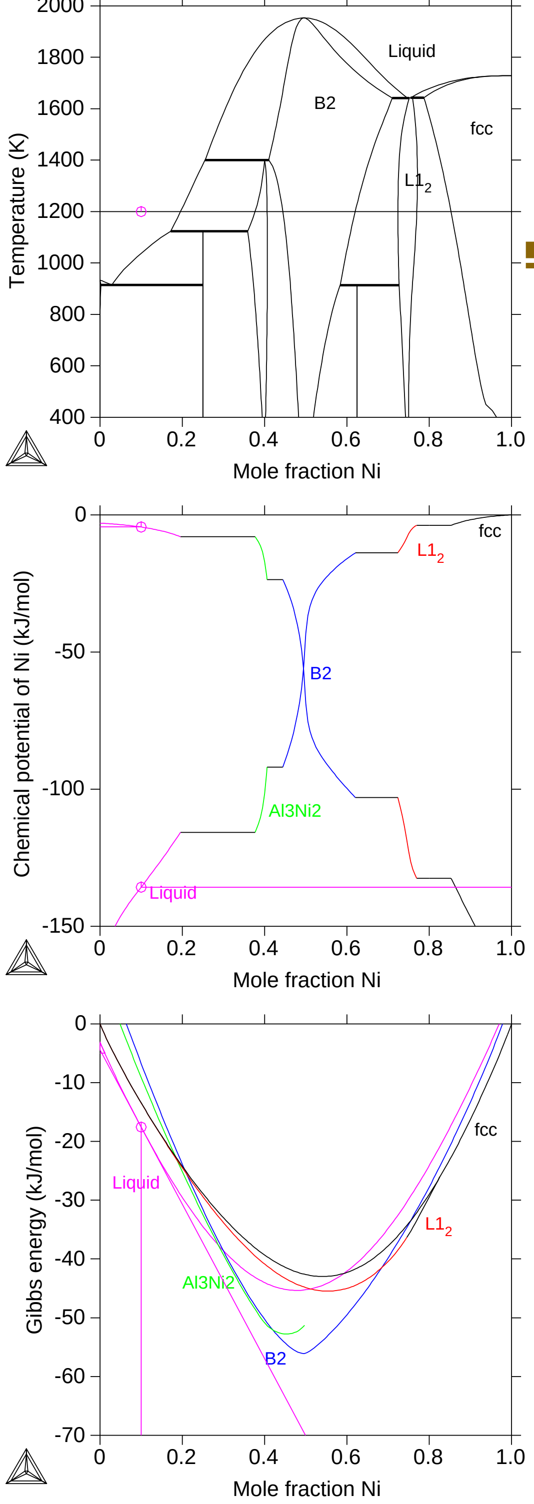
In the phase diagram a line is drawn at 1200 K.

Note that the chemical potentials are constant in two-phase regions (as this is a binary system) and these iso-activity plateaus of course coincide with the two-phase regions in the phase diagram.





How G, μ and phase diagram are connected



Here we have also added a figure at the bottom showing the modelled Gibbs energy functions for all phases in the system at 1200 K. Note that they are normally modelled for the whole composition range but the Al_3Ni_2 does not extend to pure Ni.

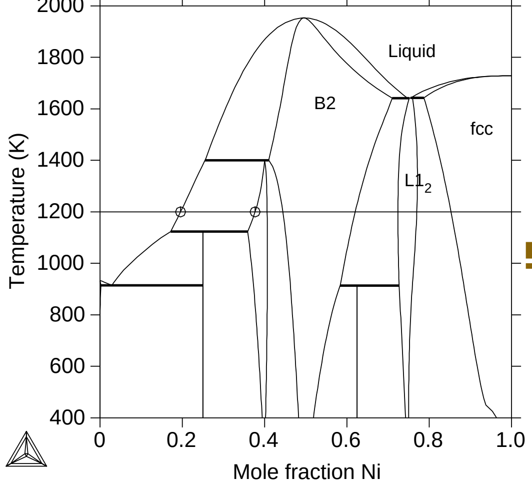
We have selected a composition at $x_{\mathrm{Ni}} = 0.1$ and drawn a tangent to the Gibbs energy curve for the stable liquid phase in the bottom figure. The end points of this tangent corresponds to the chemical potentials of the components. The end point of the tangent for Ni is below the scale of the Gibbs energy figure.

$$G_m = H_m - TS_m \tag{15}$$

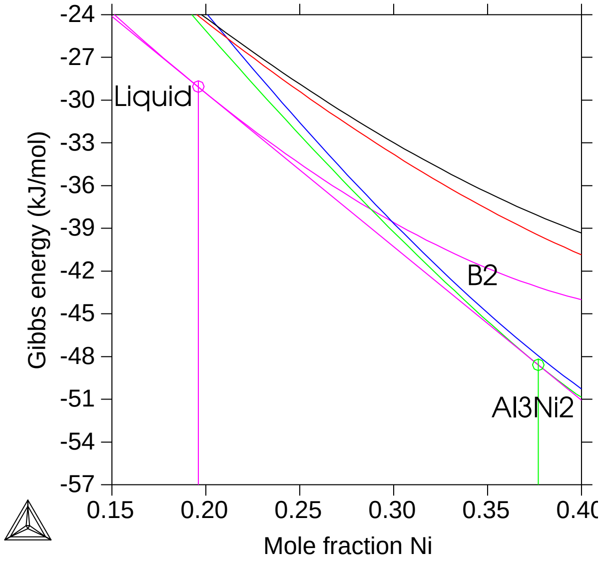
$$G_m = \sum_i x_i \mu_i \tag{16}$$

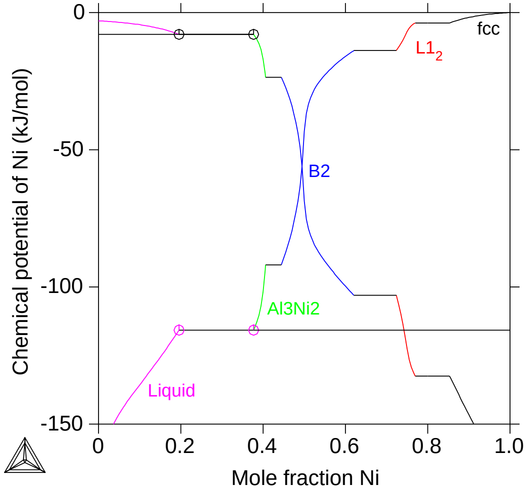
And both H_m and S_m are functions of the heat capacity.

How G, μ and phase diagram are connected

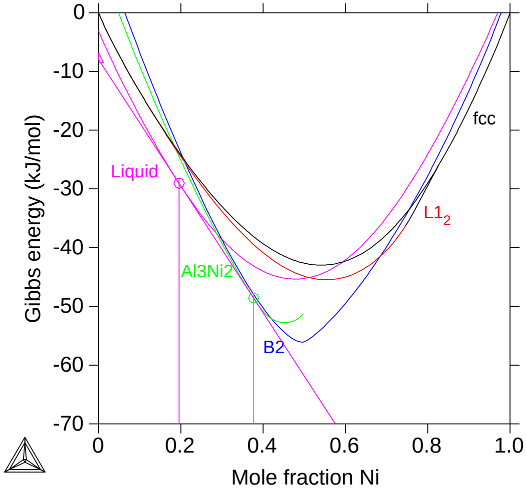


Increasing the content of Ni we come to the two-phase region between liquid and Al_3Ni_2. The chemical potential is given by the **common tangent** between the Gibbs energy curves of liquid and Al_3Ni_2 as shown in the bottom figure.





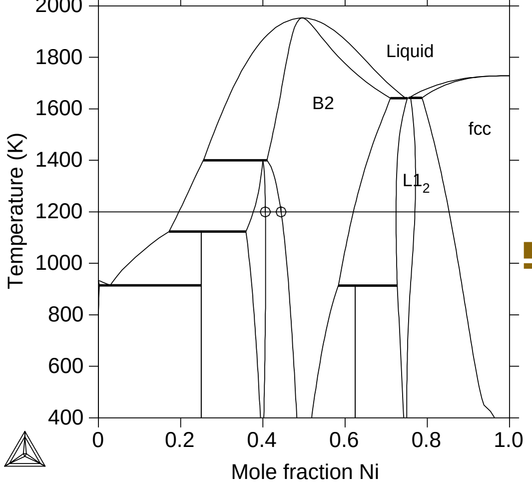
This is a magnification of the Gibbs energy curves at the two-phase region. Varying the composition across the two-phase region changes only the amounts of the phases, the composition of the phases are constant.

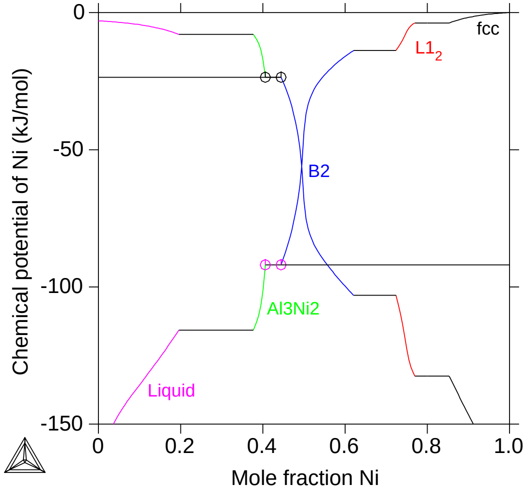


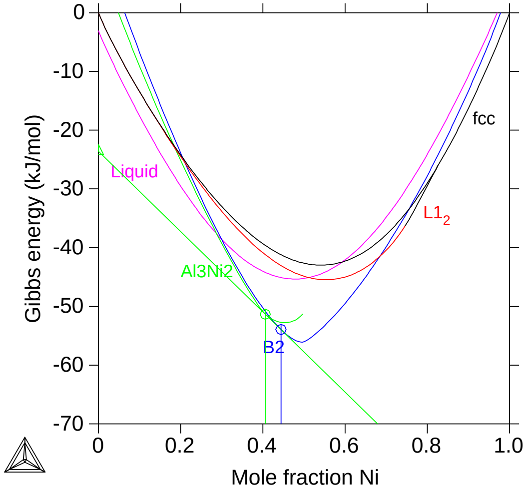
How G, μ and phase diagram are connected

On the other side of the Al_3Ni_2 phase at 1200 K we come to the two phase region between this phase and B2. As before the chemical potentials are constant in the two-phase region determined by the common tangent between the Gibbs energy curves for the Al_3Ni_2 and B2 phases.

Note that in a ternary system we must have 3 phases stable to have constant chemical potentials, in a quaternary 4 etc. This is given by the Gibbs phase rule and handelled automatically by the thermodynamic software.

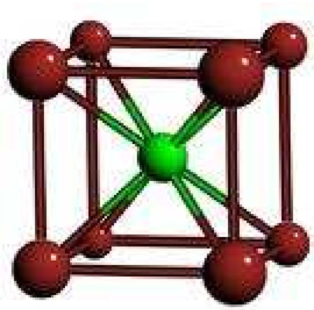






How G, μ and phase diagram are connected

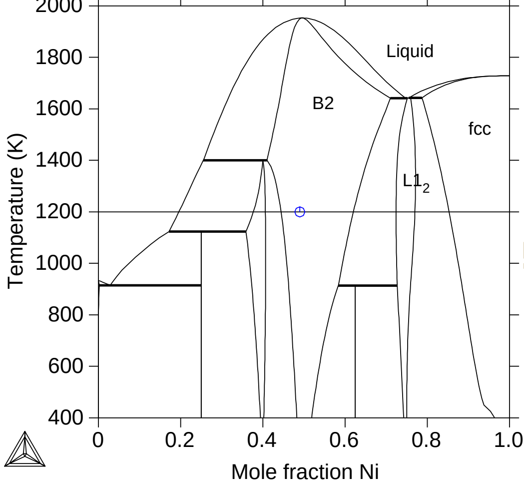
The B2 phase is an ordered form of the bcc structure and the Gibbs energy curve for the B2 phase has a pronounced minimum at the ideal composition $x_{\mathrm{Ni}} = 0.5$. The composition selected here is $x_{\mathrm{Ni}} = 0.49$.

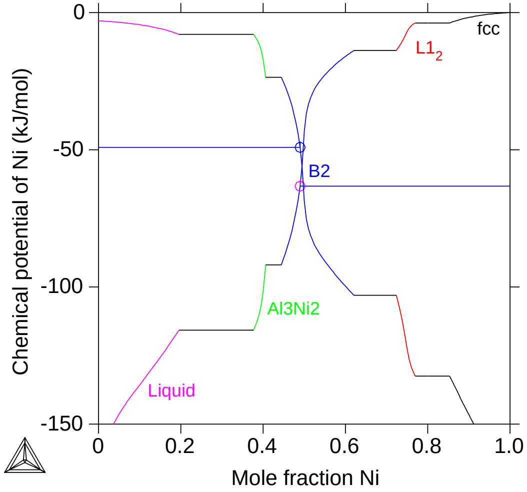


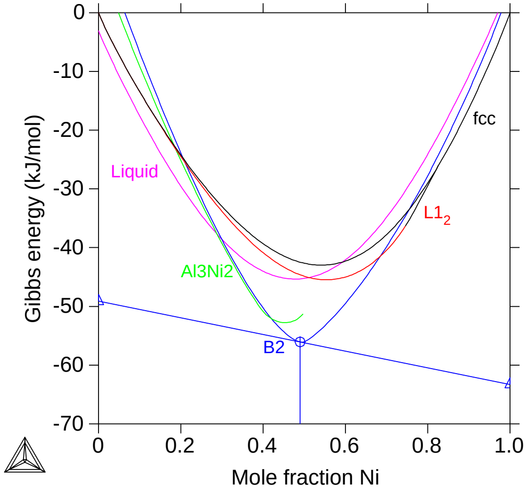
The CEF model for the B2 phase uses two identical sublattices with the same constituents on both:

$(\mathrm{Al, Ni, Va})_{0.5}(\mathrm{Al, Ni, Va})_{0.5}$

When the phase is perfectly ordred there are only Al on one sublattice and only Ni on the other. The disordered bcc has identical fractions in both sublattices.

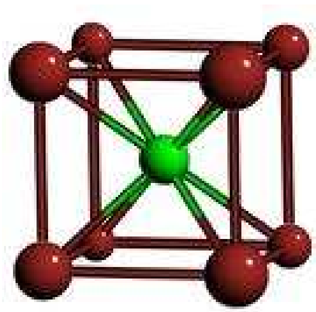






How G, μ and phase diagram are connected

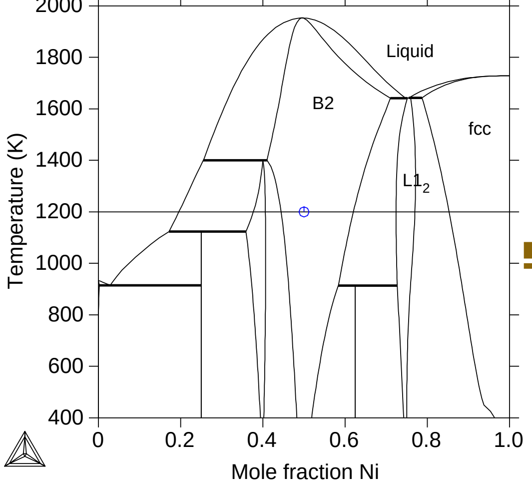
The B2 phase is an ordered form of the bcc structure and the Gibbs energy curve for the B2 phase has a pronounced minimum at the ideal composition $x_{\mathrm{Ni}} = 0.5$. The composition selected here is $x_{\mathrm{Ni}} = 0.5$.

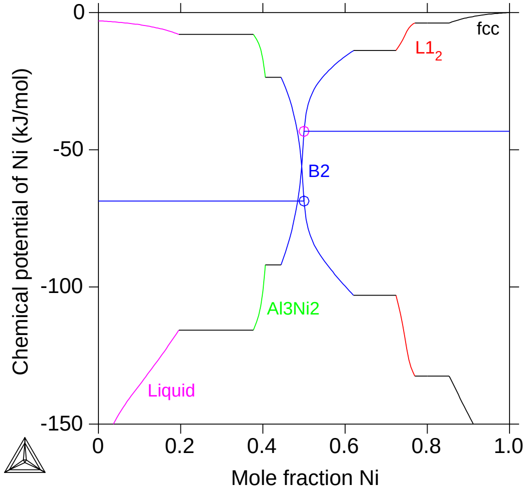


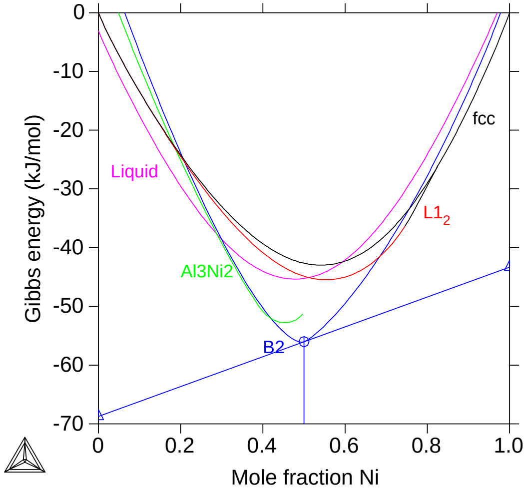
The CEF model for the B2 phase uses two identical sublattices with the same constituents on both:

$(\mathrm{Al, Ni, Va})_{0.5}(\mathrm{Al, Ni, Va})_{0.5}$

When the phase is perfectly ordred there are only Al on one sublattice and only Ni on the other. The disordered bcc has identical fractions in both sublattices.



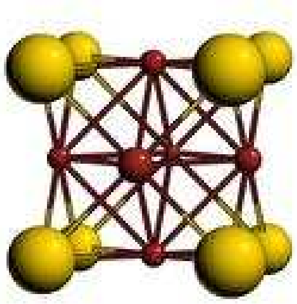




How G, μ and phase diagram are connected

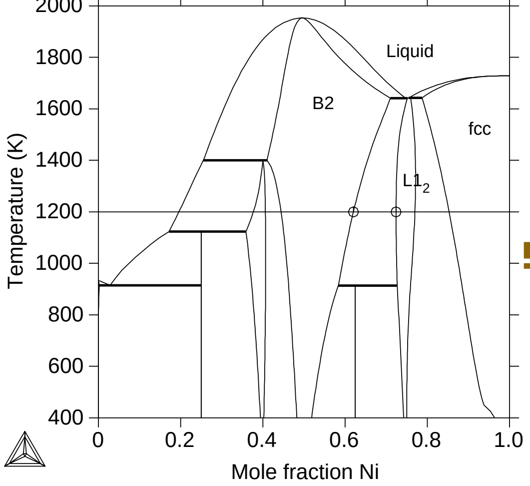
The next two-phase region is between the B2 and another ordered phase, the L1_2 which is an ordered form of the fcc structure.

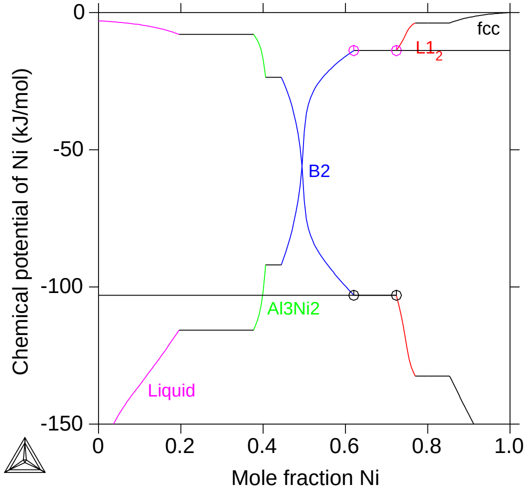
Alloys based on the L1_2 phase has good mechanical properties at high temperatures and good corrosion resistance. Many attempts are made to improve this which is the reason for the strong interest to develop thermodynamic databases for superalloys.

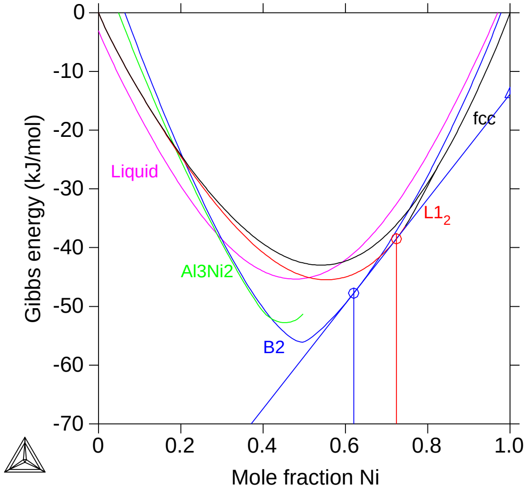


The model for the ordering in fcc is more complex than B2 and uses 4 identical sublattices:

(Al, Ni)$_{0.25}$(Al, Ni)$_{0.25}$(Al, Ni)$_{0.25}$(Al, Ni)$_{0.25}$







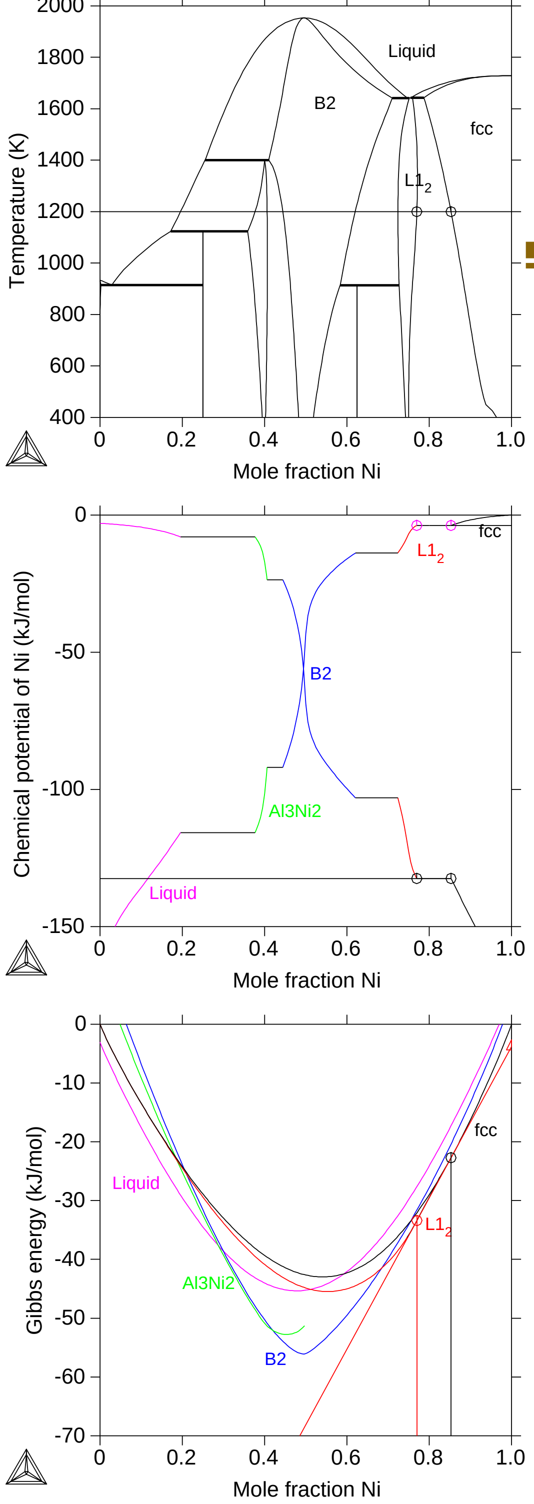
How G, μ and phase diagram are connected

Finally we reach the two-phase equilibrium between $L1_2$ and the disordered fcc. Note that the ordered and disordered forms of fcc are modelled with a single Gibbs energy function using sublattices. When the fractions of Al and Ni are the same in all sublattices the phase is disordered, otherwise it is ordered.

The Gibbs energy curves vary with temperature and this variation is fitted to the phase diagram but also the heat capacity, the entropy and thermal expansion of the phases and such properties can thus also be calculated.

Note that phase diagrams are calculated by tracing the lines where the set of phases changes. The Gibbs energy curves have been shown here just to illustrate how they determine the chemical potentials and the phase diagram.

The fact that the modelled Gibbs energy curves extend outside the stable range of the phase means they can be used to simulate phase transformations.



Chemical potentials in multicomponent systems

I think many students never come across the expression for the partial Gibbs energy of a multicomponent phase:

$$G_k = \left(\frac{\partial G}{\partial N_k}\right)_{T,P,N_j} \quad = \quad G_m + \frac{\partial G_m}{\partial x_k} - \sum_j x_j \frac{\partial G_m}{\partial x_j}$$

as many textbooks give this only for binary cases and specific models like regular solutions.

For a phase with sublattices we can in the general case calculate partial Gibbs energies only for *endmembers*, i.e. by specifying one constituent in each sublattice. That expression is

$$G_K = G_m + \sum_s \frac{\partial G_m}{\partial y_k^{(s)}} - \sum_s \sum_j y_j^{(s)} \frac{\partial G_m}{\partial y_j^{(s)}}$$

where the first sum is over the constituents given by K and the second for all constituents.

At equilibrium the partial Gibbs energies derived from the models are equal to the chemical potential and it is possible to combine the partial Gibbs energies for the endmembers to obtain the chemical potentials for the components.

Assessment of model parameters

The cumbersome part of the Calphad technique is to assess model parameters to reproduce experimental and theoretical data and it is sometimes considered as “curve fitting” by those who have never tried to do it.

They forget that a single modelling function, the Gibbs energy, is used to derive all kinds of thermodynamic data for the phase, from heat capacities, chemical potentials, heats of mixing to the bulk modulus. When the Gibbs energy functions of all the phases in a system are known we can also calculate the phase diagram.

Many different kinds of experimental data and data from first principles can be used to fit the model parameters and it means that the assesed Gibbs energy function will give consistent values for all these properties and for many more properties, for which there may be no experimental data.

Assessment of model parameters

The cumbersome part of the Calphad technique is to assess model parameters to reproduce experimental and theoretical data and it is sometimes considered as “curve fitting” by those who have never tried to do it.

They forget that a single modelling function, the Gibbs energy, is used to derive all kinds of thermodynamic data for the phase, from heat capacities, chemical potentials, heats of mixing to the bulk modulus. When the Gibbs energy functions of all the phases in a system are known we can also calculate the phase diagram.

Many different kinds of experimental data and data from first principles can be used to fit the model parameters and it means that the assesed Gibbs energy function will give consistent values for all these properties and for many more properties, for which there may be no experimental data.

Using consistent thermodynamic data is very important when simulating phase transformations because data selected or fitted independently may exhibit large inconsistencies and numerical problems when combined in the simulation software.

The assessment procedure will also highlight temperature and composition ranges where data is missing and is a guide for new experimental or theoretical work.

Assessment, Experimental data

As already mentioned each phase is modelled separately and usually for a much larger temperature and composition range than the phase is thermodynamically stable. For the metastable range theoretical data from first principles calculation is very valuable.

Calphad models, until now, does not extended below 298.15 K so the temperature dependence is often a simple polynomial in T and it is modelling the composition dependence which is the unique facility of Calphad. As already shown there are many possible ways to use CEF or similar models to describe this.

Assessment, Experimental data

As already mentioned each phase is modelled separately and usually for a much larger temperature and composition range than the phase is thermodynamically stable. For the metastable range theoretical data from first principles calculation is very valuable.

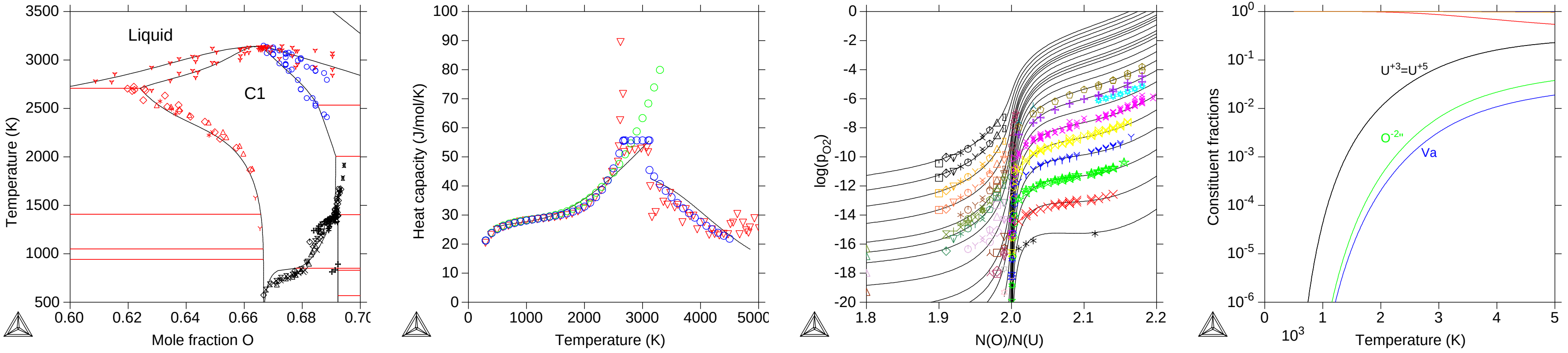
Calphad models, until now, does not extended below 298.15 K so the temperature dependence is often a simple polynomial in T and it is modelling the composition dependence which is the unique facility of Calphad. As already shown there are many possible ways to use CEF or similar models to describe this.

Experimental data can be themochemical like enthalpies of formation, transformation and mixing. Heat capacity data, activities or chemical potentials, i.e. anything that can be calculated from the Gibbs energy model. The other major source of information is the phase diagram but this provides only the relation of the Gibbs energy of two or more phases.

It is this not possible to make a reasonable assessment of a system without any enthalpy data. First principles calculations are very valuable when there are no such experimental data.

Assessment of U-O using experimental and theoretical data

This shows some of the results fitting different kinds of experimental data to the phases in the U-O system using the a CEF based model for the C1 phase and the partially ionic two-sublattice model for the liquid.



a) Phase diagram b) C_P c) P_{O_2} d) Defects

In figure a) part of the UO_2 phase diagram, in b) the heat capacity for the UO_2 composition, in c) the oxygen partial pressure for different temperatures at varying composition, all together with experimental and theoretical data. Figure d) shows the fractions of electronic and Schottky defects at UO_2 composition as function of temperature. There are no experimental data for this but first principles data for the defect energies has been used.

The important fact is that all these figures are calculated from a single Gibbs energy function for each phase. This is a unique feature of the Calphad modelling technique.

Assessment, conclusions

The assessment of themodynamic model parameters can take all kinds of thermodynamic information into account. The models may not be able to describe all details of each binary system but allows extrapolations of the main properties to real multicomponent materials.

Assessment, conclusions

The assessment of themodynamic model parameters can take all kinds of thermodynamic information into account. The models may not be able to describe all details of each binary system but allows extrapolations of the main properties to real multicomponent materials.

The modelled Gibbs energy function takes into account all relevant information that is known about the system although individual model parameters may not have any physical significance.

Assessment, conclusions

The assessment of themodynamic model parameters can take all kinds of thermodynamic information into account. The models may not be able to describe all details of each binary system but allows extrapolations of the main properties to real multicomponent materials.

The modelled Gibbs energy function takes into account all relevant information that is known about the system although individual model parameters may not have any physical significance.

Multicomponent thermodynamic databases have been used by researchers in industries and at universities for more than 20 years. The experiences are that calculations using well assessed thermodynamic databases for alloys like steel, superalloys etc with up to 10 or 12 elements give results as accurate as an experimental determination.

Assessment, conclusions

The assessment of themodynamic model parameters can take all kinds of thermodynamic information into account. The models may not be able to describe all details of each binary system but allows extrapolations of the main properties to real multicomponent materials.

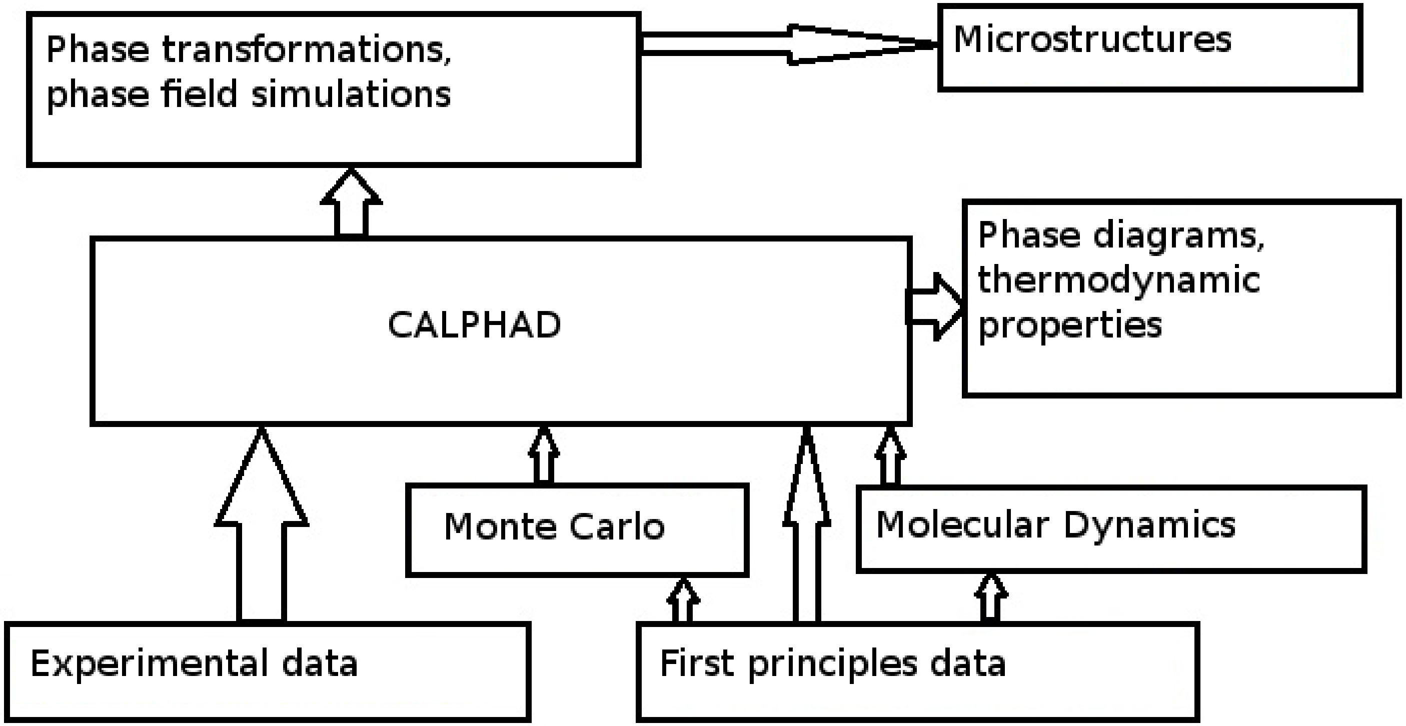
The modelled Gibbs energy function takes into account all relevant information that is known about the system although individual model parameters may not have any physical significance.

Multicomponent thermodynamic databases have been used by researchers in industries and at universities for more than 20 years. The experiences are that calculations using well assessed thermodynamic databases for alloys like steel, superalloys etc with up to 10 or 12 elements give results as accurate as an experimental determination.

It is important that the databases are well assessed by experts in the field using realistic models for the different phases. It is also important to reallize it takes time to develop a multicomponent database, often systems have to be revised two or three times before they give accurate extrapolations. This is mainly due to the fact that both the experimental and theoretical data in binary systems are often scattered and sometimes inconsistent.

Applications

The figure below illustrates how the assessed thermodynamic databases are a central link from the separate experimental and first principle data providing consistent Gibbs energy functions for different kinds of applications. The simplest applications are phase diagrams and property diagrams. Together with kinetic data on mobilities and interface energies, assessed in the same way as the thermodynamic data, we may also simulate phase transformations and microstructures.



Phase transformations,
phase field simulations

Microstructures

CALPHAD

Phase diagrams,
thermodynamic
properties

Monte Carlo

Molecular Dynamics

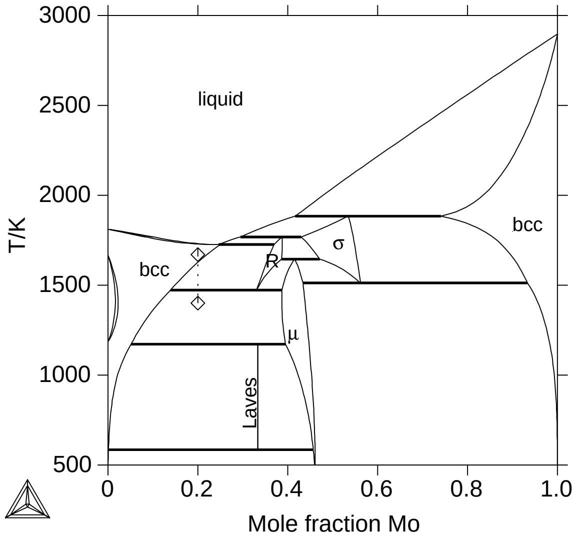
Experimental data

First principles data

Application: Thermodynamics for nucleation

We will use the Fe-Mo system as an example how the metastable extrapolation of the Gibbs energy curves can be used to provide information for simulating a phase transformation.

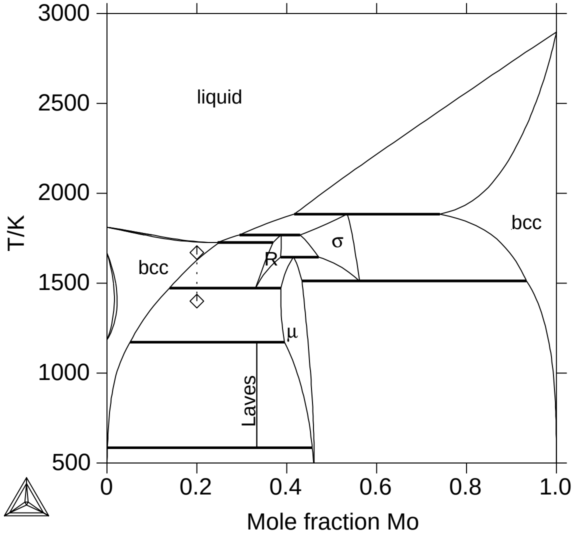
A point is marked in the phase diagram representing 20 at% Mo. If this alloy is quenched from 1700 K to 1400 K we will go from a single bcc phase to a two-phase region with bcc and μ-phase.



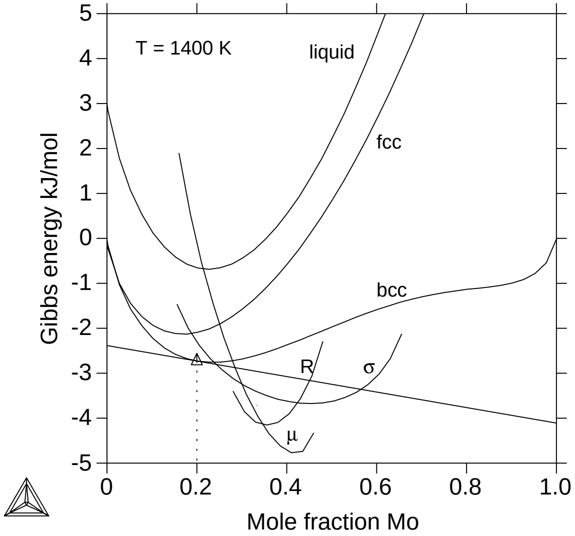
Application: Thermodynamics for nucleation

We will use the Fe-Mo system as an example how the metastable extrapolation of the Gibbs energy curves can be used to provide information for simulating a phase transformation.

A point is marked in the phase diagram representing 20 at% Mo. If this alloy is quenched from 1700 K to 1400 K we will go from a single bcc phase to a two-phase region with bcc and μ-phase.

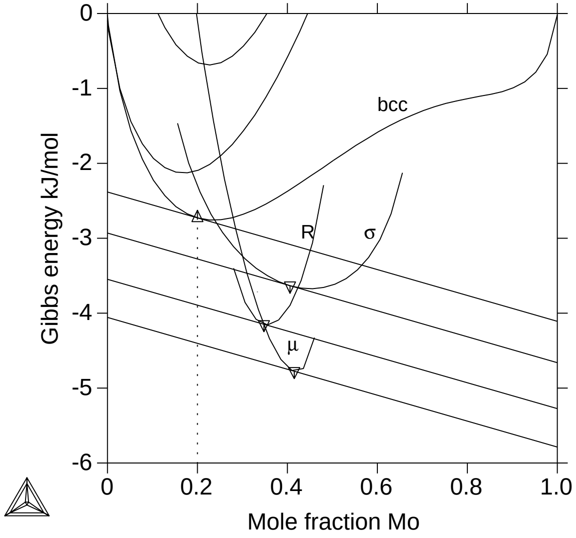


The lower figure shows the calculated Gibbs energy curves at 1400 K. If the alloy is quenched rapidly the initial state will be only bcc with the tangent indicated. But as there are other phases with lower Gibbs energy they will have a driving force for nucleation.



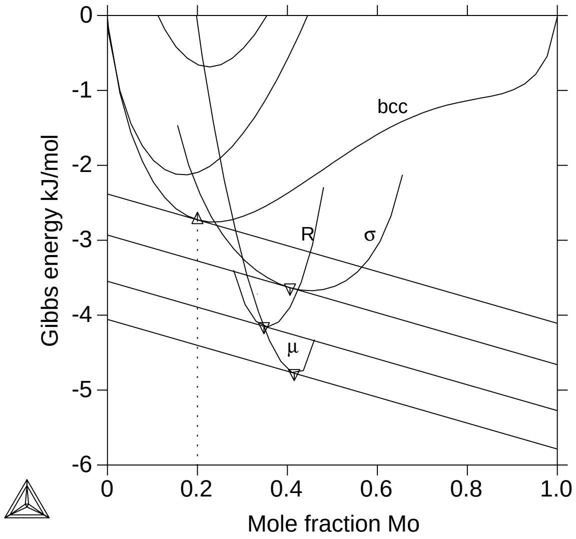
Application: Thermodynamics for nucleation

Here the interesting part of the Gibbs energy curves are magnified and we have drawn **parallel tangents** to that of the initial state. These tangent are drawn at the composition that have the largest driving force to nucleate of the phases. As can be ween it is the μ-phase that has the largest driving force.

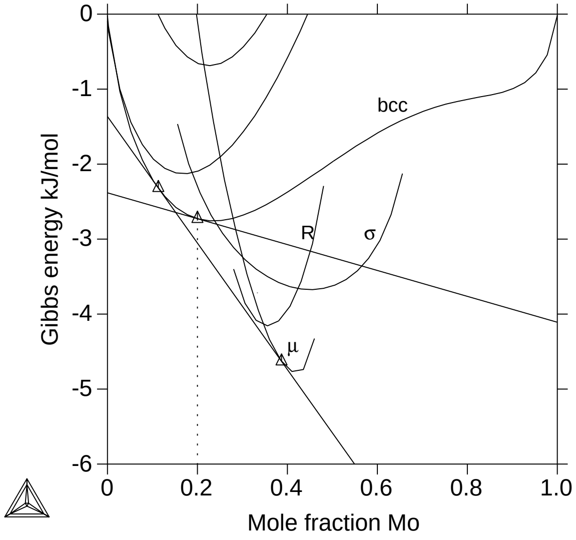


Application: Thermodynamics for nucleation

Here the interesting part of the Gibbs energy curves are magnified and we have drawn **parallel tangents** to that of the initial state. These tangent are drawn at the composition that have the largest driving force to nucleate of the phases. As can be ween it is the μ-phase that has the largest driving force.



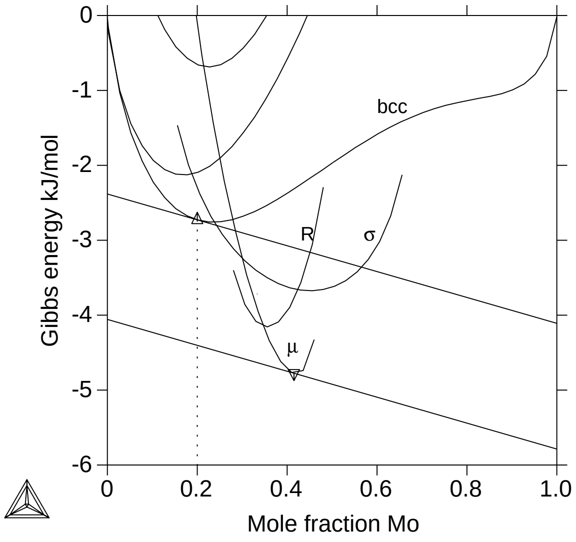
Here we have instead drawn the **common tangent** for the final state but this does not give any help to understand which phase that will nucleate first and at which composition.



Application: Thermodynamics for driving force

The driving force for nucleation is the difference in Gibbs energy between the tangent for the initial state and those constructed as parallel to this. The driving force is thus the same for all compositions.

The driving force must be large enough to overcome the energy needed to create an interface between the nucleus and the matrix phase. Inhomogenieties like grain boundaries in the matrix phase play an important role to reduce this.



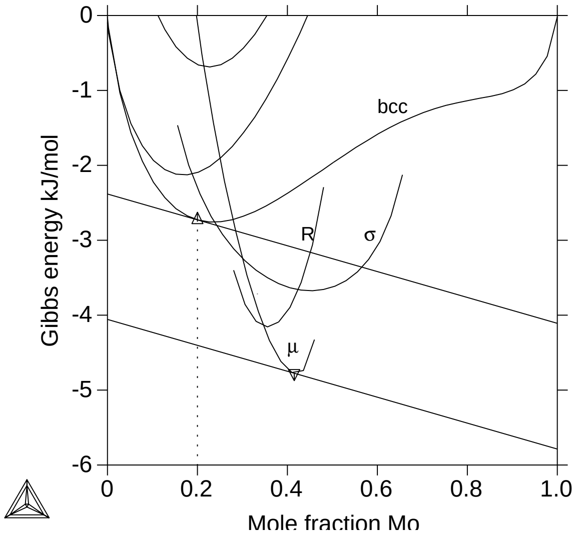
Application: Thermodynamics for driving force

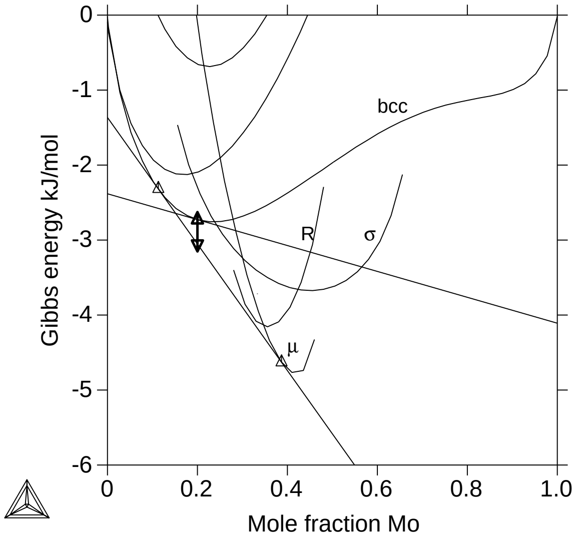
The driving force for nucleation is the difference in Gibbs energy between the tangent for the initial state and those constructed as parallel to this. The driving force is thus the same for all compositions.

The driving force must be large enough to overcome the energy needed to create an interface between the nucleus and the matrix phase. Inhomogenieties like grain boundaries in the matrix phase play an important role to reduce this.

The driving force for the whole transformation is much lower. It is the distance between the Gibbs energy at the initial state and the **common tangent** of the final state for the same composition.

For simulating the growth of the new phase we also need data for the mobilities of the elements to solve the diffusion equation. Thermodynamics provide the gradients in chemical potentials and the thermodynamic factor.





Application: Thermodynamics for diffusion

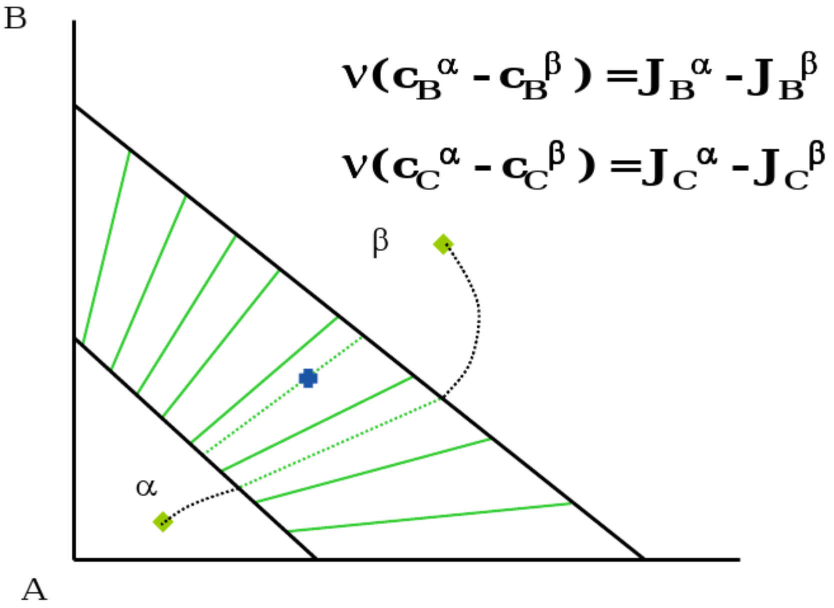
To simulate the growth of the phases one must take into account the diffusion of the components i.e. to solve the diffusion equation.

$$J_{\mathrm{B}} = -c_{\mathrm{B}} M_{\mathrm{B}} \frac{\partial \mu_{\mathrm{B}}}{\partial z} = -c_{\mathrm{B}} M_{\mathrm{B}} \frac{d\mu_{\mathrm{B}}}{dc_{\mathrm{B}}} \frac{\partial c_{\mathrm{B}}}{\partial z} \tag{17}$$

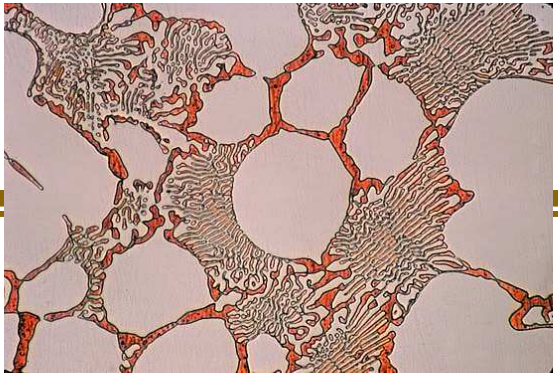
$$D_{\mathrm{B}} = c_{\mathrm{B}} M_{\mathrm{B}} \frac{d\mu_{\mathrm{B}}}{dc_{\mathrm{B}}} = x_{\mathrm{B}} M_{\mathrm{B}} \frac{\partial^2 G_m}{\partial x_{\mathrm{A}} \partial x_{\mathrm{B}}} \tag{18}$$

where $J_{\mathrm{B}}, c_{\mathrm{B}}$ and M_{B} are the flux, concentration and mobility of component B respectivly. μ_{B} is the chemical potential and z a length coordinate, D_{B} is the diffusion coefficient, G_m the Gibbs energy and x_{B} is the mole fraction.

In a binary system the tie-line at the phase interface is given by the phase diagram, or common tangent, but in a multicomponent system there are an infinite number of possible tie-lines and it is not trivial to find the one that will balance the fluxes and the movement of the phase interface.

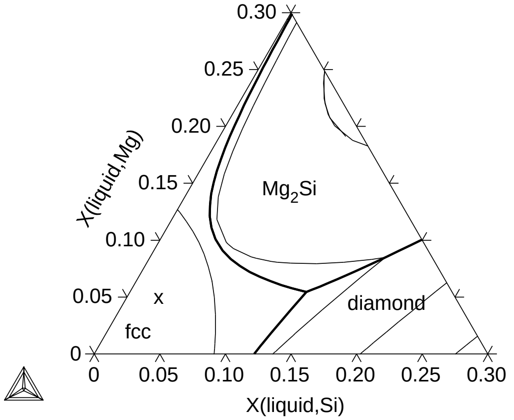


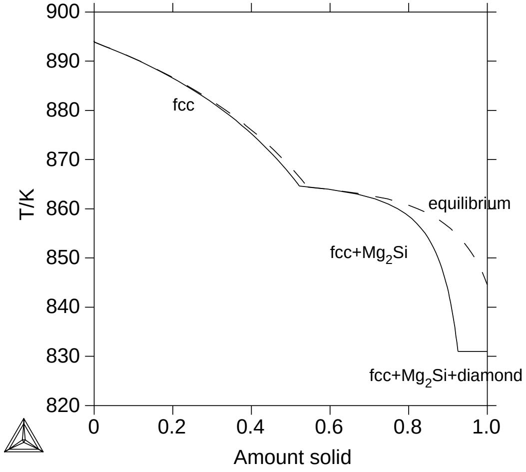
Application: Solidification



For simulating solidification we can often assume that the liquid phase have much faster diffusion that the solid phases. In the interdendritic region the “Scheil-Gulliver” model is often surprisingly good. This assumes no diffusion in the solid and that the liquid is always homogeneous. A liquidus surface for the Al-Mg-Si system in the Al corner is shown in the middle figure. The thin lines represent isothermals where the liquid is in equilibrium with one solid phase. The thick lines are univariant lines where the liquid is in equilibrium with two solid phases. There is an invariant where the liquid is in equilibrium with three solid phases.

The bottom figure shows the solidifucation curve for an alloy with 5 at% Mg and 3 at% Si. The initial solid phase is Al-rich fcc phase. There is a pronounced change in the curve when the liquid forms both fcc and Mg_2Si eutectically. Finally the invariant is reached when also some Si is formed at constant temperature.





Application: multiple length-scale simulations

There is a great interest to simulate what will happen with a material after a long time of service and in particular when we deal with materials that are difficult to handle experimentally. Detailed information on the energy of defects and other properties of materials can now be calculated by first principles methods and several attempt are made to use directly these in Monte Carlo, Molecular Dynamics and phase field simulations to find how the system will evolve with time.

Application: multiple length-scale simulations

There is a great interest to simulate what will happen with a material after a long time of service and in particular when we deal with materials that are difficult to handle experimentally. Detailed information on the energy of defects and other properties of materials can now be calculated by first principles methods and several attempt are made to use directly these in Monte Carlo, Molecular Dynamics and phase field simulations to find how the system will evolve with time.

The drawback of such simulations is that the composition dependence of the energies and properties are limited and the simulations require long computational times because they are using atomistic models.

With thermodynamic models, fitted to the first principle data as well as other experimental and theoretical data, we can describe a larger composition and temperature range of the material and can calculate the properties needed for the simulation much faster and thus simulate longer times.

Application: multiple length-scale simulations

There is a great interest to simulate what will happen with a material after a long time of service and in particular when we deal with materials that are difficult to handle experimentally. Detailed information on the energy of defects and other properties of materials can now be calculated by first principles methods and several attempt are made to use directly these in Monte Carlo, Molecular Dynamics and phase field simulations to find how the system will evolve with time.

The drawback of such simulations is that the composition dependence of the energies and properties are limited and the simulations require long computational times because they are using atomistic models.

With thermodynamic models, fitted to the first principle data as well as other experimental and theoretical data, we can describe a larger composition and temperature range of the material and can calculate the properties needed for the simulation much faster and thus simulate longer times.

The assessment procedure needed to develop the Calphad databases requires time and effort but the results can be used in many simulations for varying conditions, much more flexibly than with any other materials modelling technique.

Concluding remarks

The thermodynamic databases of Calphad type have already established their usefulness for many materials like steels, superalloys, ceramics etc. for industrial as well as scientific applications.

Concluding remarks

The thermodynamic databases of Calphad type have already established their usefulness for many materials like steels, superalloys, ceramics etc. for industrial as well as scientific applications.

The thermodynamic databases are in no way competitive with first principle calculations, they are simply the only possible way to combine data from such calculations with the available experimental data of different types. Of course models can be improved as well as the assessment procedure and we welcome all scientists who are interested in improving the modelling and participating in the assessement of a multicomponent thermodynamic databases.

Concluding remarks

The thermodynamic databases of Calphad type have already established their usefulness for many materials like steels, superalloys, ceramics etc. for industrial as well as scientific applications.

The thermodynamic databases are in no way competitive with first principle calculations, they are simply the only possible way to combine data from such calculations with the available experimental data of different types. Of course models can be improved as well as the assessment procedure and we welcome all scientists who are interested in improving the modelling and participating in the assessement of a multicomponent thermodynamic databases.

The cost and efforts to develop accurate multicomponent databases are not insignificant. But it will pay back its cost many times by reducing the need for many other kinds of calculations and costly experimental work for improving the knowledge of current fuels as well as investigating new. A Calphad database is an invaluable tool for simulations to understand materials processes, how the material will behave in service as well as what may happen in extreme situations.

End of presentation

Thank you

Activity coefficients problem

$$\begin{aligned}
\mu_i &= RT\ln(\gamma_i x_i) \\
G_m = \sum_i x_i \mu_i &= RT \sum_i x_i \left(\ln(x_i) + \ln(\gamma_i)\right) \\
\mu_k = \left(\frac{\partial G}{\partial N_k}\right)_{T,P,N_j} &= G_m + \frac{\partial G_m}{\partial x_k} - \sum_j x_j \frac{\partial G_m}{\partial x_j} \\
\frac{\partial G_m}{\partial x_j} &= RT(\ln(x_j) + \ln(\gamma_j)) + RT + RT \sum_i \frac{x_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x_j} \\
\mu_k/RT &= \sum_i x_i \ln(\gamma_i x_i) + \ln(\gamma_k x_k) + 1 + \sum_i \frac{x_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x_k} - \\
&\quad \sum_j x_j(\ln(\gamma_j x_j) + 1) - \sum_j x_j \sum_i \frac{x_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x_j} \\
&= \ln(\gamma_k x_k) + \sum_i \frac{x_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x_k} - \sum_j x_j \sum_i \frac{x_i}{\gamma_i}\frac{\partial \gamma_i}{\partial x_j} \\
&= \ln(\gamma_k x_k) + \sum_i \frac{x_i}{\gamma_i}\left(\frac{\partial \gamma_i}{\partial x_k} - \sum_j x_j \frac{\partial \gamma_i}{\partial x_j}\right)
\end{aligned}$$

Integral binary excess

$$
\begin{aligned}
G_m &= RT\sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j L_{ij} \\
\frac{\partial G_m}{\partial x_k} &= RT(\ln(x_k) + 1) + \sum_i x_i L_{ik} \\
\mu_k &= RT\sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j L_{ij} + RT(\ln(x_k) + 1) + \sum_i x_i L_{ik} - \\
&\quad \left(RT\sum_i x_i(\ln(x_i) + 1) + \sum_i \sum_j x_i x_j L_{ij} \right) \\
&= RT\ln(x_k) + \sum_i x_i L_{ik} - \sum_i \sum_{j>i} x_i x_j L_{ij} \\
RT\ln(\gamma_k) &= \sum_i x_i L_{ik} - \sum_i \sum_{j>i} x_i x_j L_{ij} \\
G_m &= \sum_k x_k \mu_k = RT\sum_k x_k \ln(x_k) + \sum_k \sum_i x_i x_k L_{ik} - \sum_k x_k \sum_i \sum_{j>i} x_i x_j L_{ij} \\
&= RT\sum_k x_k \ln(x_k) + \sum_i \sum_{j>i} L_{ij}
\end{aligned}
$$

Integral binary excess

$$
\begin{aligned}
G_m &= RT(x_A \ln(x_A) + x_B \ln(x_B)) + x_A x_B L_{AB} \\
\frac{\partial G_m}{\partial x_A} &= RT(\ln(x_A) + 1) + x_B L_{AB} \\
\mu_A &= RT(x_A \ln(x_A) + x_B \ln(x_B)) + x_A x_B L_{AB} + RT(\ln(x_A) + 1) + x_B L_{AB} - \\
&\quad (RT x_A(\ln(x_A) + 1) + x_A x_B L_{AB} + RT x_B(\ln(x_B) + 1) + x_B x_A L_{AB}) \\
&= RT \ln(x_A) + x_B(1 - x_A) L_{AB} = RT \ln(x_A) + (1 - x_A)^2 L_{AB} \\
RT \ln(\gamma_A) &= x_B(1 - x_A) L_{AB} \\
\gamma_A &= \exp(x_B(1 - x_A)\frac{L_{AB}}{RT}) \\
G_m &= x_A \mu_A + x_B \mu_B \\
&= RT x_A \ln(x_A) + x_A x_B(1 - x_A) L_{AB} + RT x_B \ln(x_B) + x_B x_A(1 - x_B) L_{AB} \\
&= RT(x_A \ln(x_A) + x_B \ln(x_B)) + x_A x_B(1 - x_A + 1 - x_B) L_{AB} \\
&= RT(x_A \ln(x_A) + x_B \ln(x_B)) + x_A x_B L_{AB}
\end{aligned}
$$