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

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OpenCalphad, Gif sur Yvette, France

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Outline

- Third generation Calphad databases
  - Extend the Gibbs energy model to 0 K using an Einstein model.
  - Model the glas transition of the liquid.
  - Improve models for magnetism and other physical phenomena.
  - Metastable solid pure elements at very high T.
- Modeling liquids including the glass transition
- Extrapolation of solid phases to high T

Thermodynamic properties at low T

These are modeled with an Einstein function, a polynomial in T with no T and $T\ln(T)$ terms to make $C_P = S = 0$ at $T = 0$ K for a stable phase α:

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where SERF means “Stable Element Reference Function” and a_0, a_1 etc. are fitted to $S_{298}, H_{298} - H_0$, experimental and DFT data for C_P in the stable range. R is the gas constant and $\theta^{\alpha}_{\mathrm{A}}$ the Einstein T. ${}^{\mathrm{mgn}}G_{\mathrm{A}}$ is the magnetic term.

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$$G^{\gamma}_{\mathrm{A}} - G^{\alpha}_{\mathrm{A}} = b_0 + b_1 T \qquad (4)$$

is used to determine the $\theta^{\gamma}_{\mathrm{A}}$ in for the allotrope:

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Stable solid phases which are not perfect crystals, like inverse spinel and solutions, can have a non-zero configurational entropy at 0 K.

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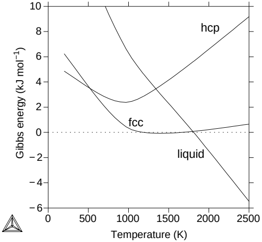

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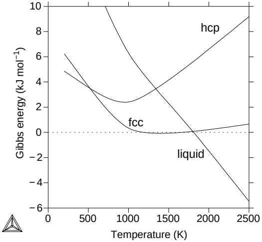

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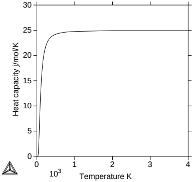
Including heat capacity data made the Calphad databases useful for new applications in process modelling, simulations of phase transformations, energy conversion etc.

Fitting polynomials

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



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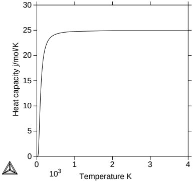

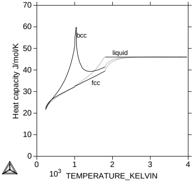

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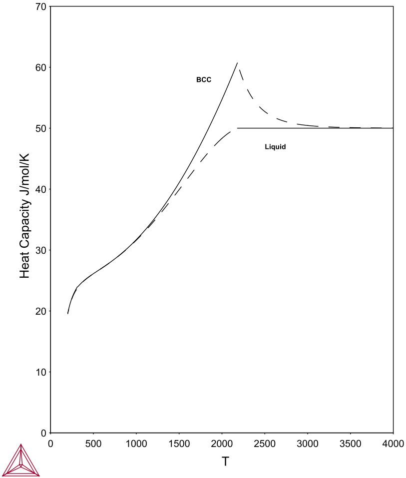
But here are the stable and extrapolated heat capacity curves and magnetism for the different forms of pure Fe. So there is still a lot of theory to develop before one can match reality and avoid fitting polynomials.

Breakpoints at melting T

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



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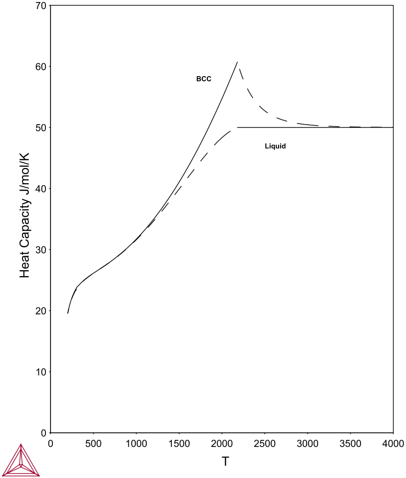

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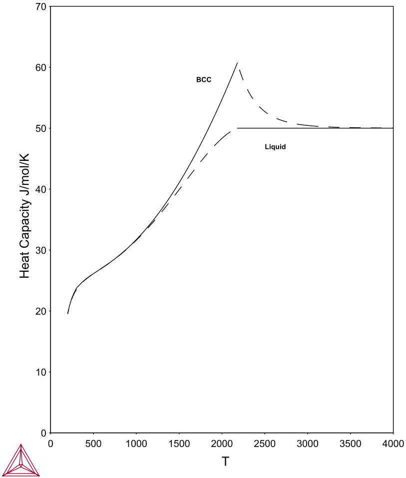

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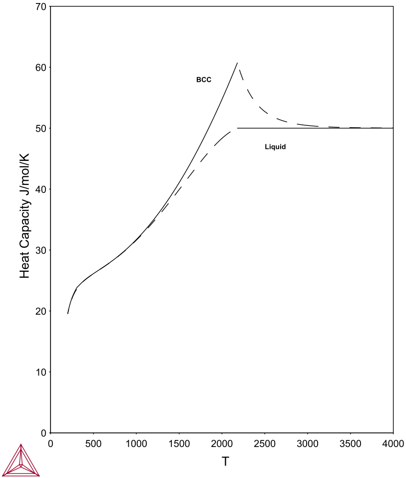

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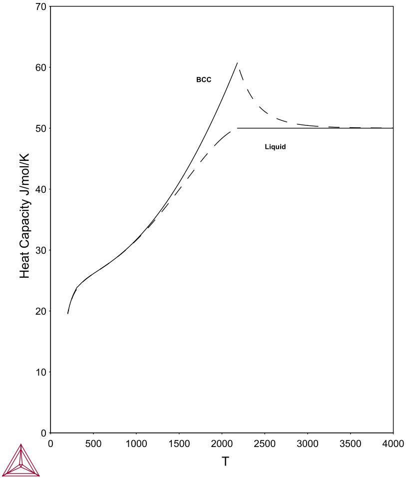

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- It is also a problem (at least for geologists) that the breakpoint is a fixed value and does not vary with P.

General acceptance

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

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

General acceptance

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

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Extrapolating the liquid to low T

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

$$^\circ G_{\mathrm{A}}^{\mathrm{liq}} = G_{\mathrm{A}}^{\mathrm{am}} - RT\ln(1+\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT})) \tag{6}$$

where $G_{\mathrm{A}}^{\mathrm{am}}$ describes the low T amorphous state and $G_{\mathrm{A}}^{\mathrm{2state}}$ describes the transition to and the difference between the liquid and the amorphous state.

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where ${}^{\mathrm{Ein}}G$ is the Einstein function (eq. 2 above), $\theta_{\mathrm{A}}^{\mathrm{am}}$ is the Einstein T of the amorphous state. c_0, c_1, c_2 are coefficients describing the the amorphous state stability relative solid phases which must be fitted to the melting T and melting enthalpy.

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It has now been agreed that **the amorphous state will have $S > 0$ at $T = 0$ K** and thus $G_{\rm A}^{\rm am}$ can have a linear term with T (as it is not a perfect crystalline state). But the heat capacity should be zero at $T = 0$ K.

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At high T in the liquid state we must have $\exp(-\frac{G_{\mathrm{A}}^{\mathrm{2state}}}{RT}) >> 1$, i.e. eq. 6 becomes:

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

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

$$G_{\mathrm{A}}^{\mathrm{2state}} = d_0 + d_1T + d_2T\ln(T) + \cdots \tag{7}$$

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

An example

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

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

$$G_{\mathrm{A}}^{\mathrm{2state}} = d_0 + d_1 T - 25 T \ln(T)$$

- A recommendation is that the heat capacity of the liquid at very high T should approach $3R$.
- The values d_0 and d_1 can be fitted to have a smooth heat capacity for the transition from amorphous to liquid state below the melting T, here assumed to be around 2000 K.

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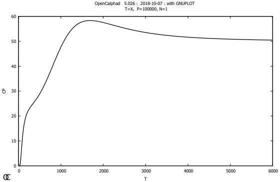
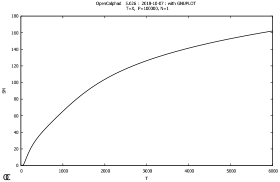
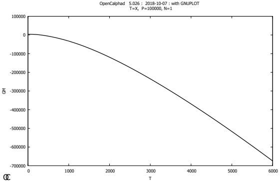
$$G^{\mathrm{2state}} = 100 + 180T - 25T\ln(T):$$







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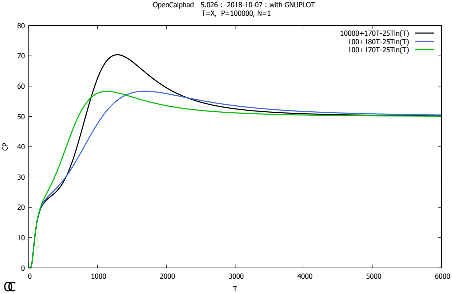

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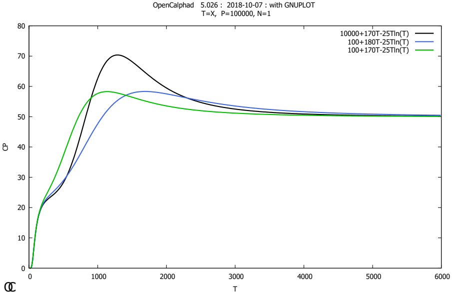

There will always be a "hump".
With a smaller d_1 coefficient and larger d_0 the "hump" maximum will grow.
With smaller C_P term the d_1 coefficient will be less positive.

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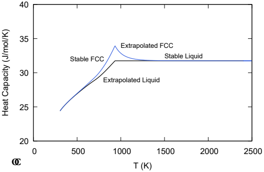

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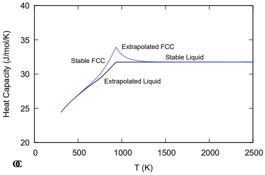

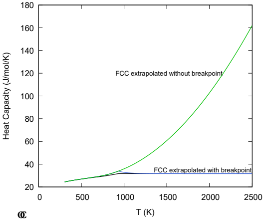

and in this figure the heat capacity of the solid fcc has been extrapolated without the breakpoint

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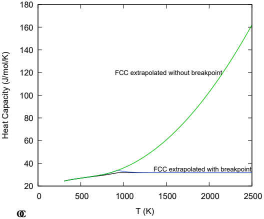

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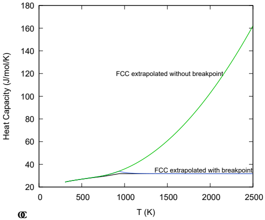

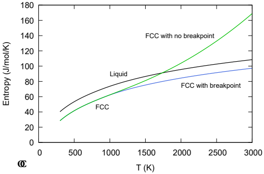

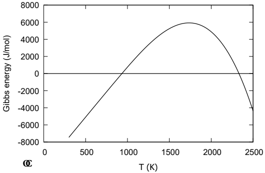

The entropy will increase drastically and around 1600 K the entropy of the fcc will be larger than the liquid.

The point of crossing is also shown as the maximum of the Gibbs energy difference between the liquid and the solid and it means the extrapolated solid will become stable around 2300 K.

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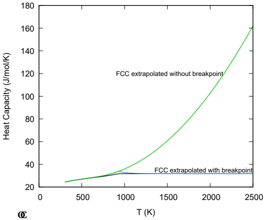
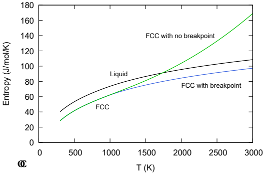
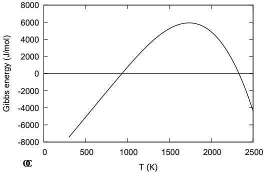
For a pure element or compound it has been accepted that a solid phase with an entropy larger than the liquid must be considered as unstable or even nonexistant and never be allowed to be stable.

Starting from the pure fcc Al without breakpont







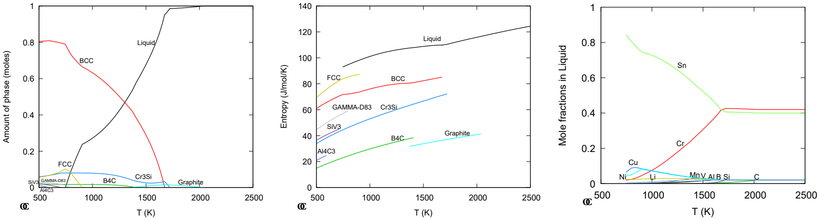
The entropy will increase drastically and around 1600 K the entropy of the fcc will be larger than the liquid.

The point of crossing is also shown as the maximum of the Gibbs energy difference between the liquid and the solid and it means the extrapolated solid will become stable around 2300 K.

The question is if this can be applied to a multicomponent system.

Extrapolation of the metastable solids to high T

I have made many calculations for systems with 10-15 elements with the databases I have access to and this is one set of such calculations for an 11 component alloy with about 40% Cr and 40% Sn and 2% of 9 other elements with varying T.



In the left figure the amount of different phases, in the middle the entropy of the phases and in the right the composition of the liquid at varying T.

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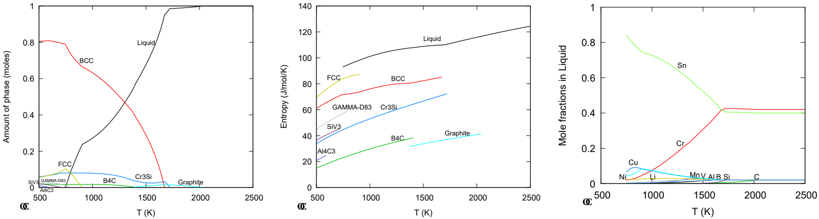

In the left figure the amount of different phases, in the middle the entropy of the phases and in the right the composition of the liquid at varying T. The interesting fact is that the liquid always has the highest entropy even when its composition varies.

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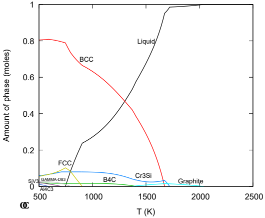
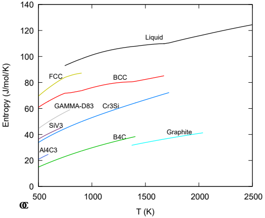
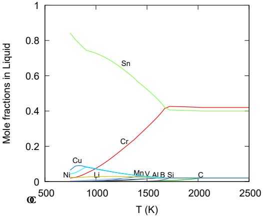




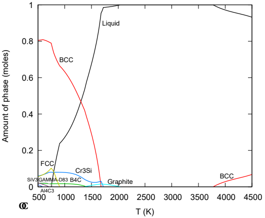


In the left figure the amount of different phases, in the middle the entropy of the phases and in the right the composition of the liquid at varying T. The interesting fact is that the liquid always has the highest entropy even when its composition varies.

One may make a proposition that a solid with higher entropy than the liquid must be unstable.

Extrapolation of the metastable solids to high *T*

The previous figues were calculated with the SGTE breakpoints. If I remove the breakpoints I get the following phase fraction diagram. The bcc phase becomes stable at very high *T*.



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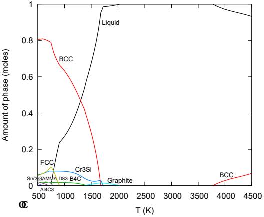
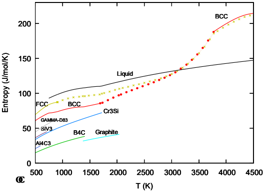
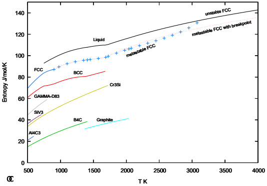


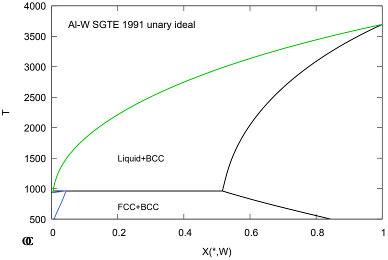




In the middle figure we can see that the entropy of the bcc and fcc phases increase at high T and the bcc becomes stable soon after the entropy of these phases has become higher than the liquid entropy. In the right hand figure the equi-entropy criterion has removed the bcc and fcc phases from the caculation when the entropy of is higher than the liquid. This prevents them reappearing at high T.

Extrapolation of the metastable solids to high T

I believe the "equi-entropy criterion" is a useful method to handle extrapolation of metastable solids also in multicomponent systems. But there are some restrictions that must be implemented in the expressions used to extrapolate the Gibbs energy for low melting elements like Al. For a system like Al-W a phase diagram calculated with the SGTE 1991 unaries look like:



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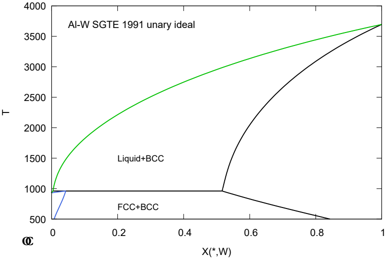
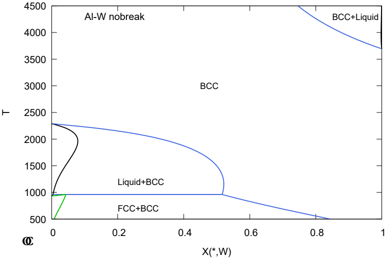
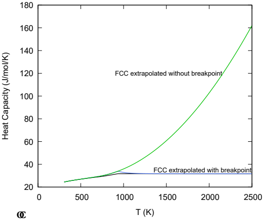


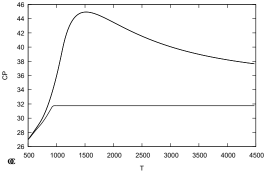


and the right hand figure show the diagram if we remove the breakpoint. The criteria of equal entropy is not useful here as the bcc phase is in fact stable on the W side.

Extrapolation of the metastable solids to high T

There must be a restriction on the extrapolation of the metastable solid for example like in this diagram. In this case the extrapolated fcc is changed to another expression at 1100 K which will approach a constant value at high T.





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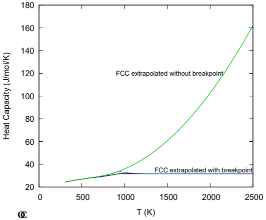

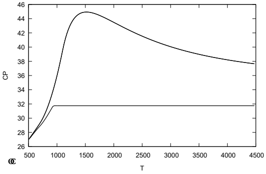

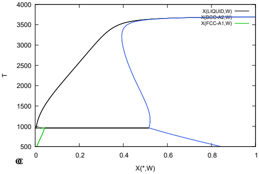

With a heat capacity like this we get a phase diagram that can be used to assess interaction parameters to fit experimental data.

The very high hump on the heat capacity curve can be modified by a more restrictive fit to the solid heat capacity close to the melting.

The equi-entropy criterion is still needed to avoid that the BCC becomes stable at even higher *T*.

Thanks for listening