Thermodynamic assessments

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Calcul Thermodynamique

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Outline

- What is a thermodynamic assessment?
- Why a thermodynamic assessment?
- How to performe a thermodynamic assessment?
- When is it finished?

What is a thermodynamic assessment ?

- It provides
  an equation of the Gibbs energy
  for all the phases stable
  in a simple system under consideration versus
  - temperature,
  - composition (constitution),
  - and pressure.

What is a thermodynamic assessment ?

- It is constituted of three main steps:
  1. All the experimental information (phase diagram, crystallography and thermodynamic properties) as well as all theoretical results on the system or on the phases stable in the system are critically assessed.

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  2. A model is defined for each phase taking into account in particular the crystallographic knowledge.
  3. The parameters of the models are assessed - in a least squares method - in order to fit the selected information, in particular phase diagram and thermodynamic properties.

Why a thermodynamic assessment ?

- This system is a key system for a material, for an aplication.
- This description is needed to extend a complex database.
- This system is not well known and the thermodynamic description will help to plan experiments.
- There is a new piece of information on this system.
- There is no thermodynamic description of the system.
- The available description is not describing some important features.
- The model used in available description is not consistent with my database.
- There is a new model to test.

Why a thermodynamic assessment ?

- It allows end users
  - to calculate phase diagram, the nature of the phases, their composition and the thermodynamic properties in this system what ever the conditions, under stable or metastable equilibrium,
  - to better take into account thermodynamic features when modelling the kinetic evolution in the system,
  - to built complex thermodynamic databases.

How to perform a thermodynamic assessment ?

1. Reading : critical assessement of experimental and theoretical knowledge on the system and phases under consideration.
2. Modelling : defines a model for each phase based on step 1.
3. Optimising : gives values to the parameters of the models defined at step 2 fitting the data extracted from step 1.

Exhaustive bibliography

of experimental works

- phase equilibria
- thermodynamic properties
- crystallography

as well of theoretical studies

- previous Calphad
- ab initio

in system

- under consideration
- similar ones
- others where the phases under consideration appear

In order to

- get experimental values that will be compared to calculated values in the optimising step
- estimate the uncertainties of the different datasets
- define the models

Caution

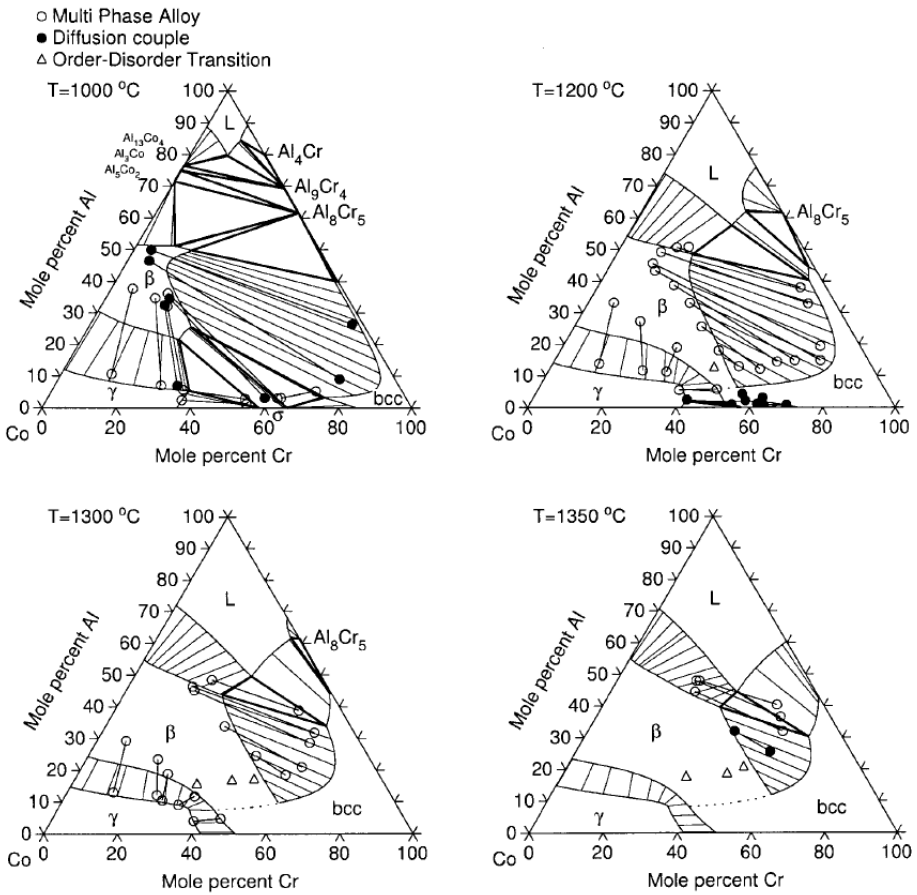
- Available critical assessments
  - make this task easier but
  - should not avoid reading original papers.
- Experimental results should be used as rough as possible, without post processing and transformation but
- in the real world,
  - equilibrium is reached after a certain time,
  - calibration is made - or not - by human being,
  - there are systematic errors,
  - the starting materials have some impurities,
  - and may react with the crucible or with the atmosphere.
- *If you have two conflicting datasets then either one or the other may be correct or both may be wrong.* Bo Jansson.
- It is not because two datasets agree that they are right.
- Disregarding data is a big pain when they are scarce.

Experimental techniques

- phase diagram
  - metallography (qualitative)
  - X-Ray : identification of the phases, limits of one phase fields
  - microprobe : composition of the phases
  - DTA : liquidus, solidus, solvus, invariant reactions, ...
- thermodynamic properties
  - calorimetric measurements ($H - H(T_0)$, c_P, ΔH_f, ...)
  - mass spectrometry (partial pressure, activity)
  - emf
  - isopiestic
- crystallography (X-Ray, neutrons)
  - identification of the phases
  - number of sites, multiplicity, occupation $\Rightarrow$ models
  - site occupancies
  - molar volumes

Difficulties to assess uncertainty when scarce data

Al-Co-Cr



K. Ishikawa *et al.*, *Ber. Buns. / Phys. Chem.*, 1998, 102(9) 1206-1210.

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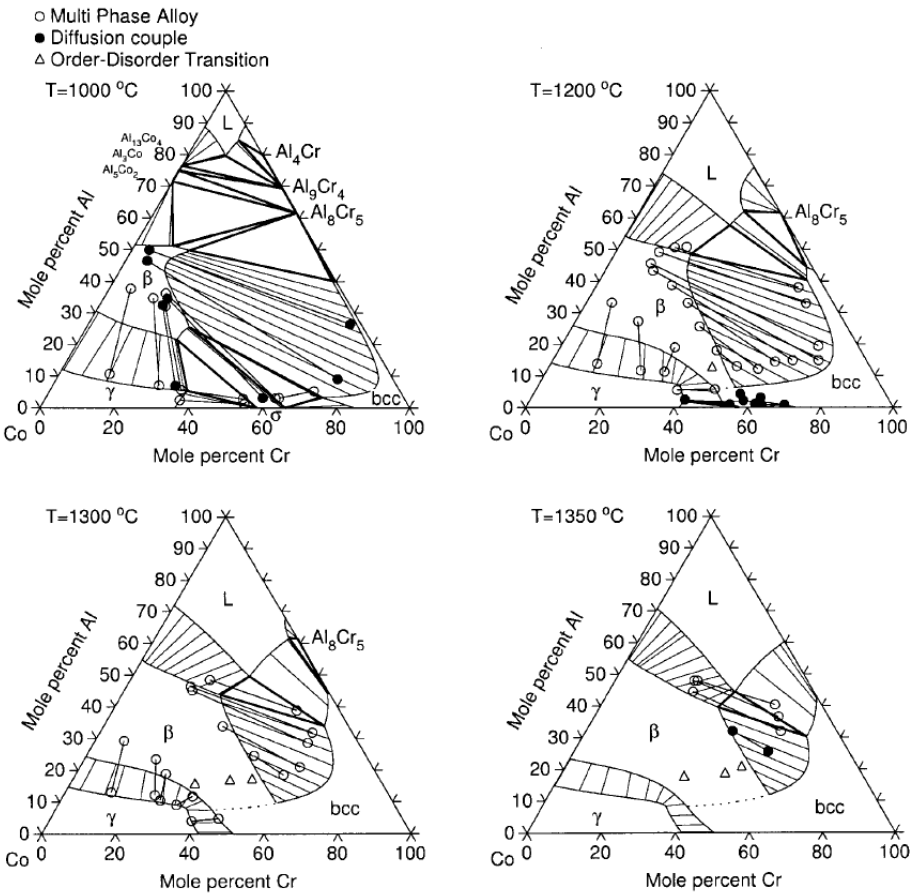

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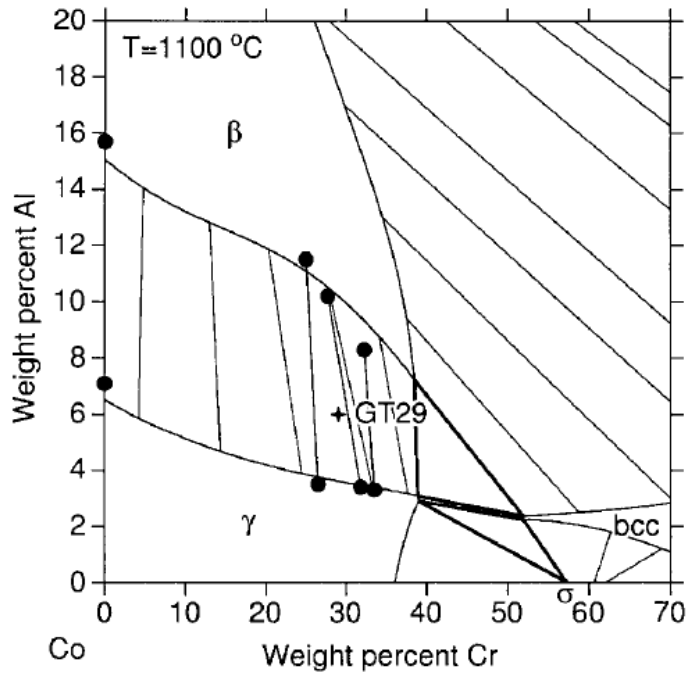


T. Gómez-Acebo *et al.*, JPEDAV (2004) 25:237-251

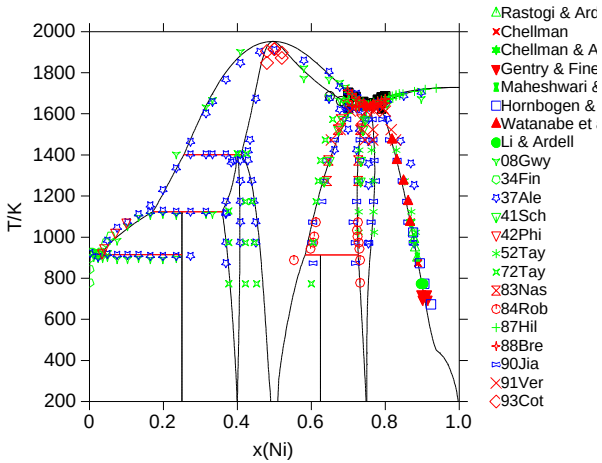
Using ab initio

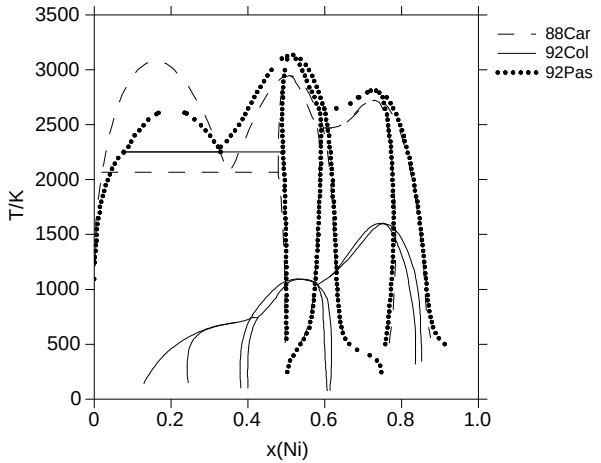
of interest in particular in metastable fields

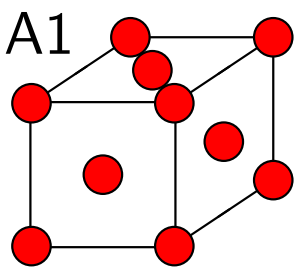
- topology, ex: Al-Ni fcc ordering
- total energy, ex: Nb-Ni μ
- better lattice stability for pure elements in highly metastable phases (Laves, σ, μ, $\cdots$). The end of 5000+GHSER !
- volume,
- ...

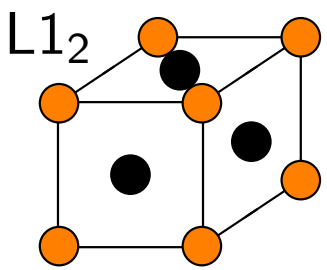
Topology of metastable phase diagram

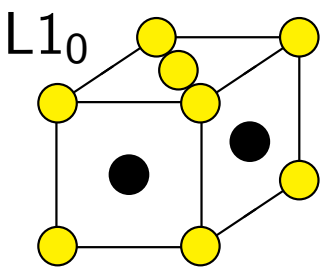
Al-Ni

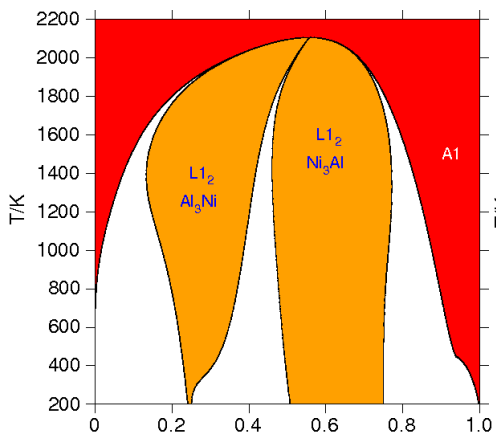


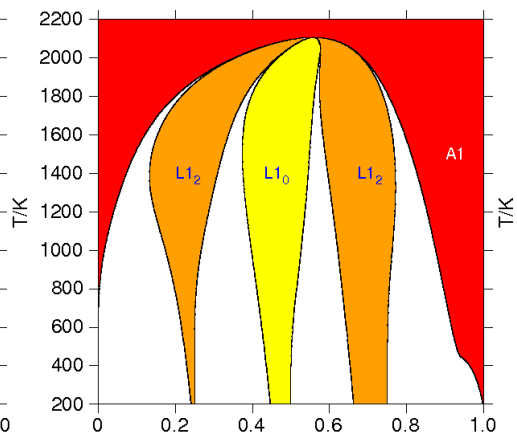


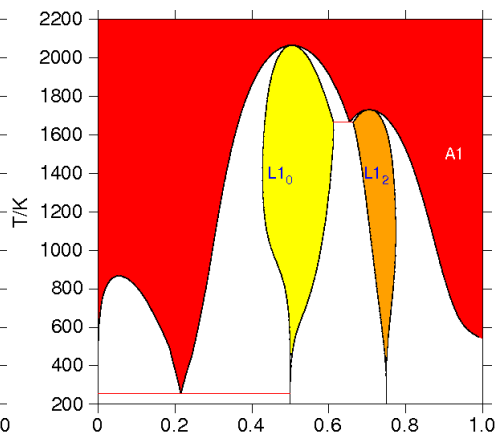






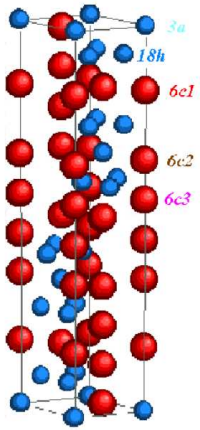




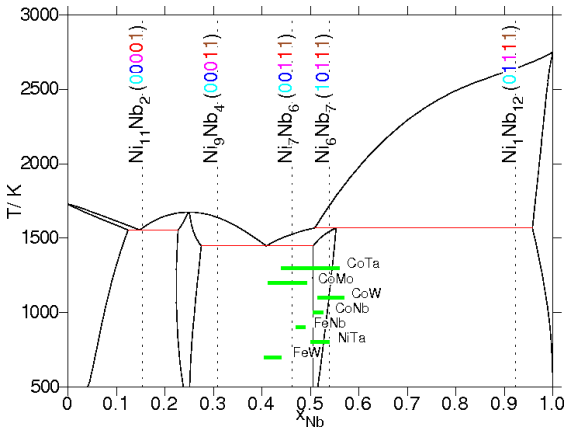


Total energy

Nb-Ni



Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	3a	6c1	6c2	6c3	18h
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe



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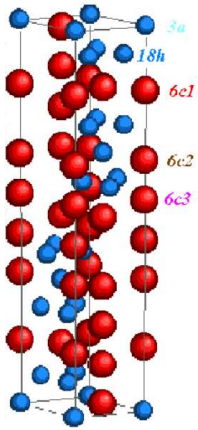

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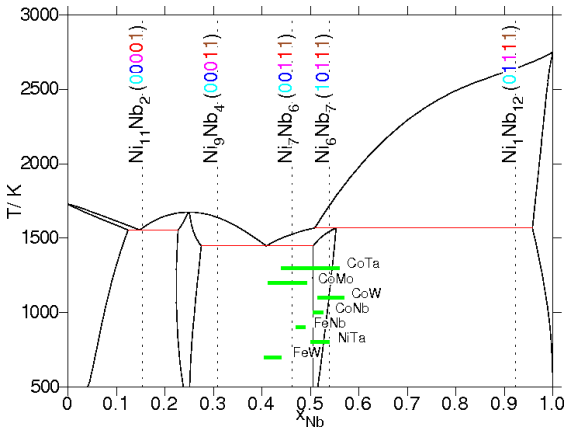
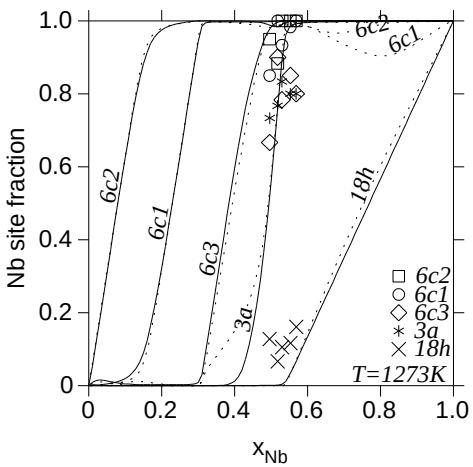
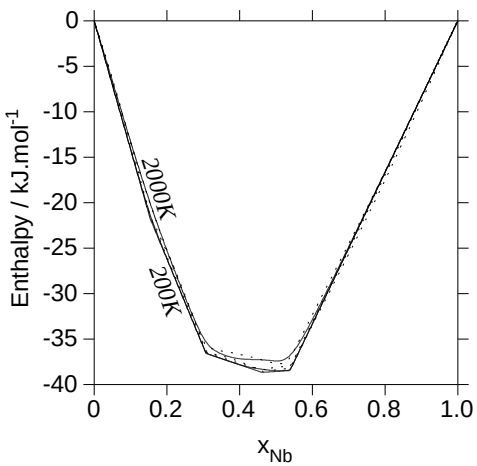
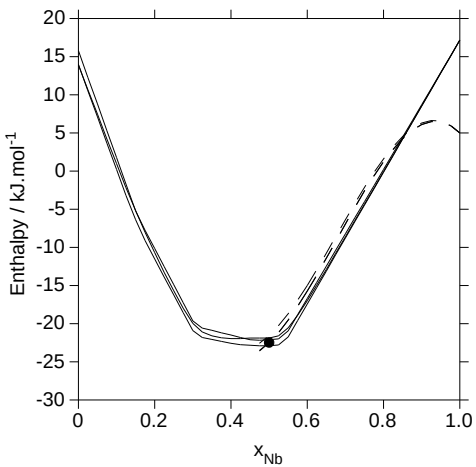


VASP 32 compounds + CEF







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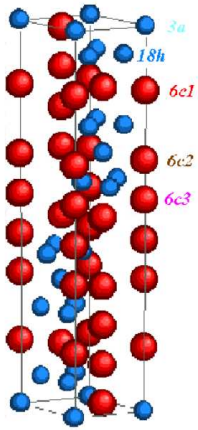

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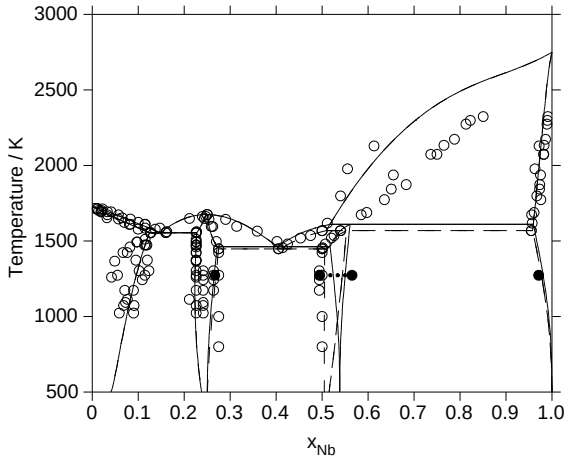

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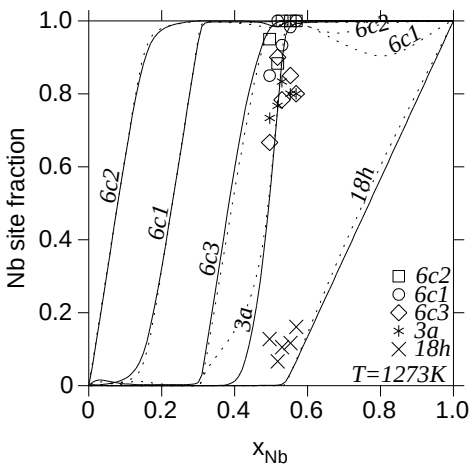
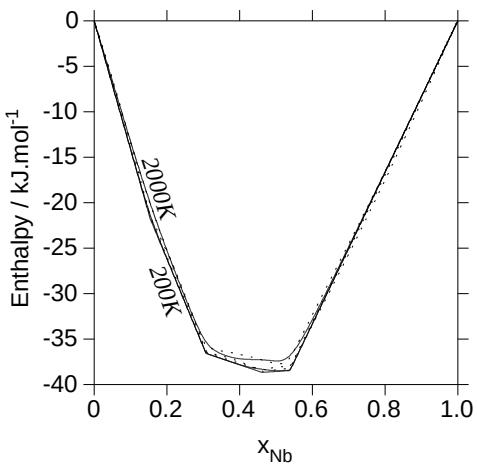
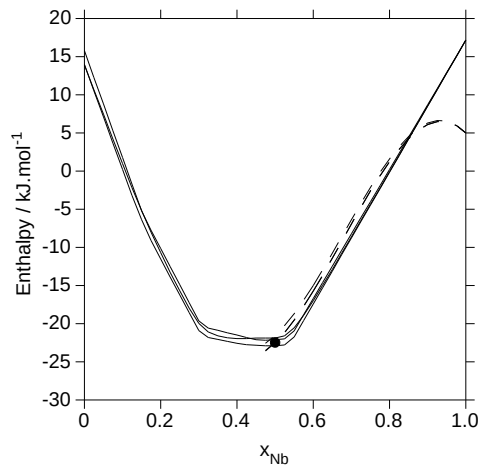






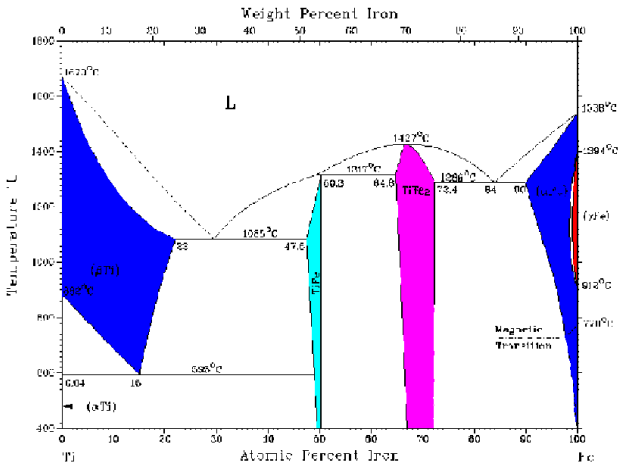
What is the thermodynamic modelling of a phase?

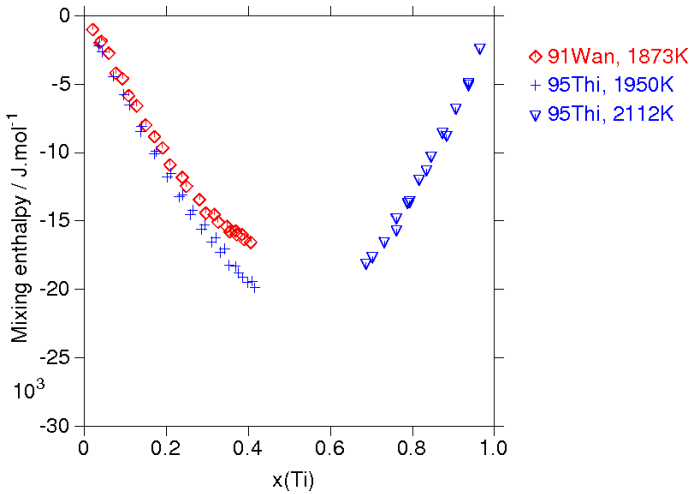
- It defines the species contributing to the entropy of the phase and to its non-stoichiometry and the way they mix.
- It defines the general equation of the Gibbs energy of the phase whose parameters will later be given values by least square method for instance but it could also be just by trial and error or by advanced estimates like ab initio.
- It is based on the experimental knowledge of the phase, in particular from its crystallography but can also be based on the thermodynamic behaviours (H or μ_i vs x or T) or ab initio results on point defects.
- It is better to consider the knowledge of the phase in many different systems rather than in the only one under consideration in order to use a model that will be able to extrapolate in multicomponent systems.
- It requires a good knowledge of the thermodynamic models.

Examples

- To model the liquid phase in Fe-Ti, the substitutional model (Fe,Ti) and the associate model (Fe,FeTi,Fe) induce different equations.
- To model the Laves C14 phase with the CEF $(Fe,Ti)_2(Fe,Ti)$ or $(Fe,Ti)_3(Fe,Ti)_2(Fe,Ti)$ induce different equations
- To model the A2/B2 or A1/L12 phases with a single equation induces different equations and constraints on the parameters.

Fe-Ti liquid


Weight Percent Iron
L
Atomic Percent Iron
Ti
Fe


Mixing enthalpy / J.mol-1
x(Ti)
91Wan, 1873K
95Thi, 1950K
95Thi, 2112K

Fe-Ti C14

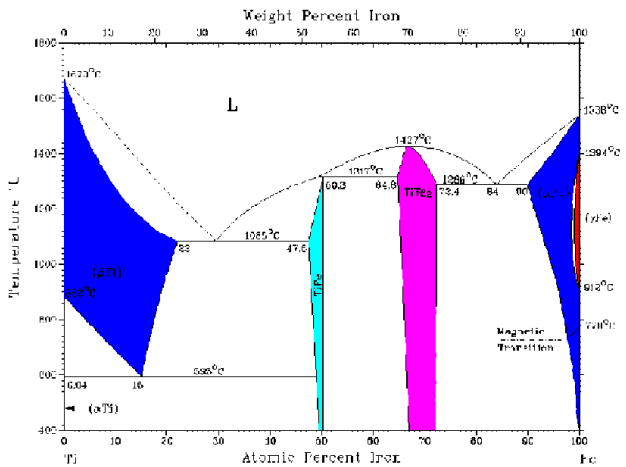
$(Fe,Ti)_2(Fe,Ti)$ or $(Fe,Ti)_3(Fe,Ti)(Fe,Ti)_2$?

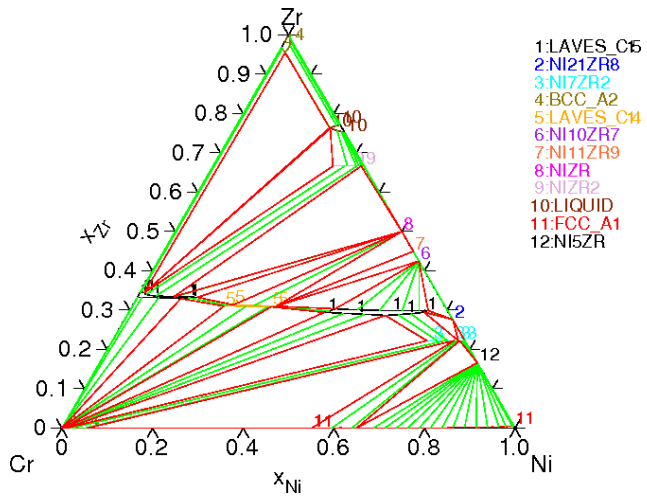
Crystallographie

Prototype $MgZn_2$ ***StrukturBericht*** $C14$ ***Pearson*** $hP12$ ***Groupe d'espace*** $P6_3/mmc$

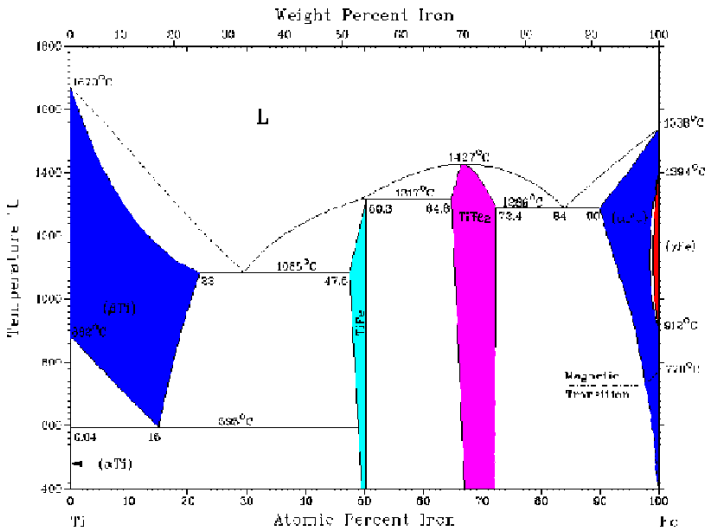
Caractéristiques des différents sites pour le prototype

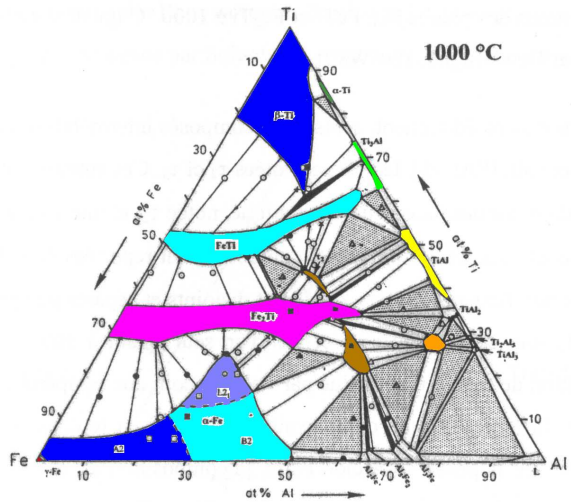
Occupation	Multiplicité	Wickoff	Symétrie
Zn	6	h	mm2
Mg	4	f	3m.
Zn	2	a	-3m.



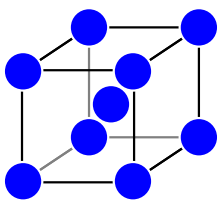


A2/B2 modelling

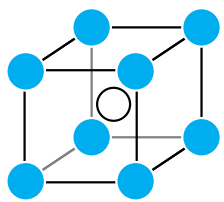




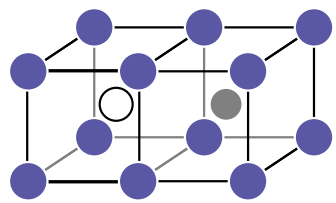
A2



B2



$L2_1$



In order to be able to describe the 2nd order transition between the A2, B2 and $L2_1$ phases in the ternary system Al-Fe-Ti, the A2 and B2 phases have to be describe with 4SL in the binary system Fe-Ti.

Optimising

- Setting up a description
  - elements
  - phases
  - functions
  - parameters
  - initial values of variables used in functions and parameters
- Defining and computing equilibria
- Defining uncertainties and weights
- Least squares optimisation
- Comparing with all data available
- Verifying metastable equilibria
- Rounding, final checking

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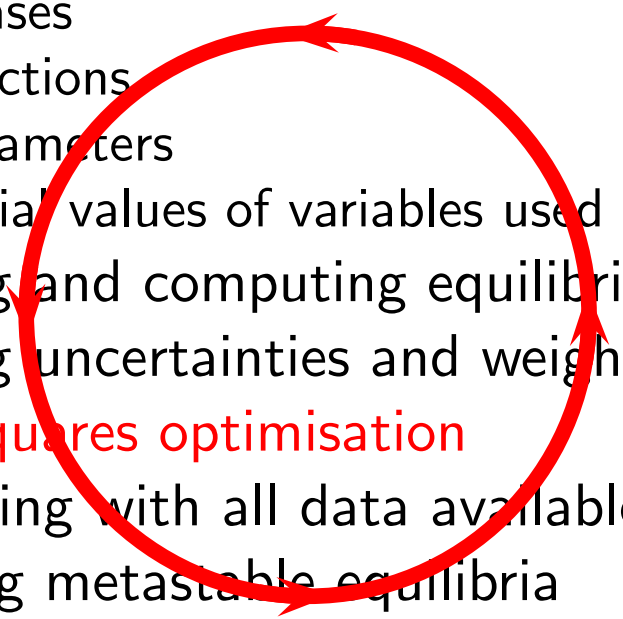


Why initial values?

To be able to calculate equilibria.

Even if sofwares provide a different may to work, an optimisation requires to calculate the properties to be fitted. It may be rather tricky in particular when dealing with ordering transitions.

To go faster

Imagine that you are searching x such as $x^2=2\pm0.1$ by numerical iteration. Whatever the numerical algorithm used, you will get your answer faster if you start from 1.4 than if you start from 0.

To keep in mind the physical meaning of the variables assessed, their effect on the overall resulting description.

The sum of squares to minimize is a complex hull that may show several local minima. Starting with physically meaningful values may avoid to fall in unrealistic local minima.

What initial values?

Substitutional solution

$$G_m^\alpha - \sum_{i=A,B} x_i^\alpha H_i^{SER_i}(T_0) = \sum_{i=A,B} x_i^\alpha (G_i^\alpha - H_i^{SER_i}(T_0)) + RT \sum_{i=A,B} x_i^\alpha \ln x_i^\alpha + x_A^\alpha x_B^\alpha L_{A,B}^\alpha$$

$$\begin{aligned} \Delta G_{mix}^\alpha &= G_m^\alpha - \sum_{i=A,B} x_i^\alpha G_i^\alpha \\ &= RT \sum_{i=A,B} x_i^\alpha \ln x_i^\alpha + x_A^\alpha x_B^\alpha L_{A,B}^\alpha \end{aligned}$$

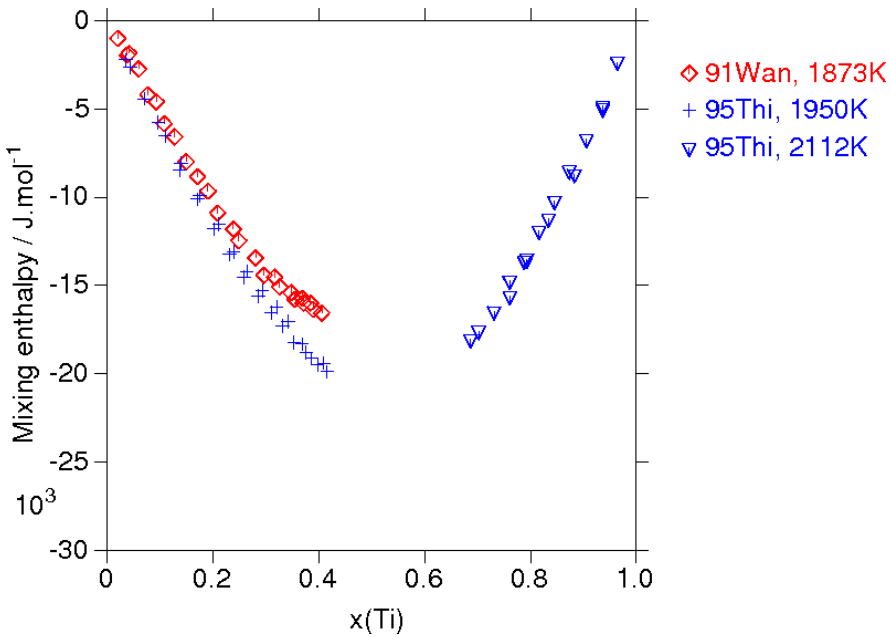
What initial values?

Substitutional solution

If $L^{\alpha}_{A,B} = a^{\alpha}_{A,B} + b^{\alpha}_{A,B} T$

$$\Delta H^{\alpha}_{mix} = x^{\alpha}_{A}\, x^{\alpha}_{B}\, a^{\alpha}_{A,B}$$

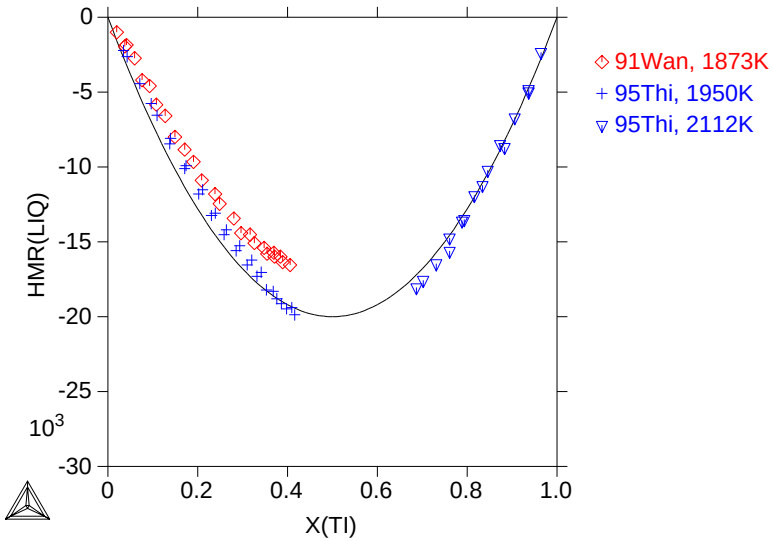
- What is the experimental value for ΔH^{α}_{mix} at $x^{\alpha}_{i} = 0.5$?
- What initial value could be guessed for $a^{\alpha}_{A,B}$?

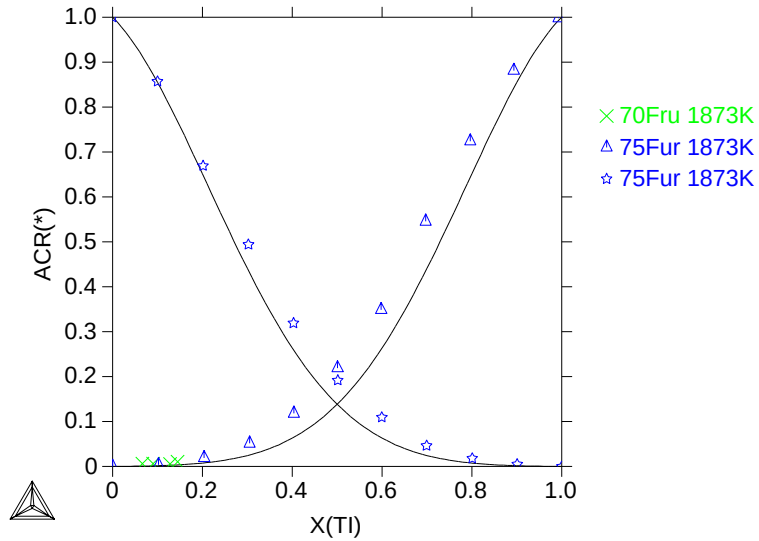


What initial values?

Substitutional solution

$$a^{\alpha}_{A,B} = -80\,000$$





What initial values?

Liquid substitutional solution

When no experimental value is available

Miedema's estimate

- original paper
- dos ptp by Hari Kumar
- windows by Xingqiu Chen
  http://www.tssc.univie.ac.at/xingqiu/xingqiu.html

provide reasonable starting values.

What initial values?

Solid solution

When no experimental thermodynamic value is available

- The phase diagram, and in particular the equilibria with the liquid phase, often allow reasonable starting values.

What initial values?

Solid solution

When no experimental thermodynamic value is available

- The phase diagram, and in particular the equilibria with the liquid phase, often allow reasonable starting values.
- For phases with little stability range,
  - do not optimise lattice stabilities,
  - use few interaction parameters, if possible related to another solution in the system for which you have more information,
  - avoid zero as interaction parameter.

What initial values?

Compound

- If some experimental c_p, $\Delta H_f(298)$, $\Delta S_f(298)$ available and c_P already assessed as $c_P = c_0 + c_1 T + c_{-2} T^{-2} + c_2 T^2 + \cdots$

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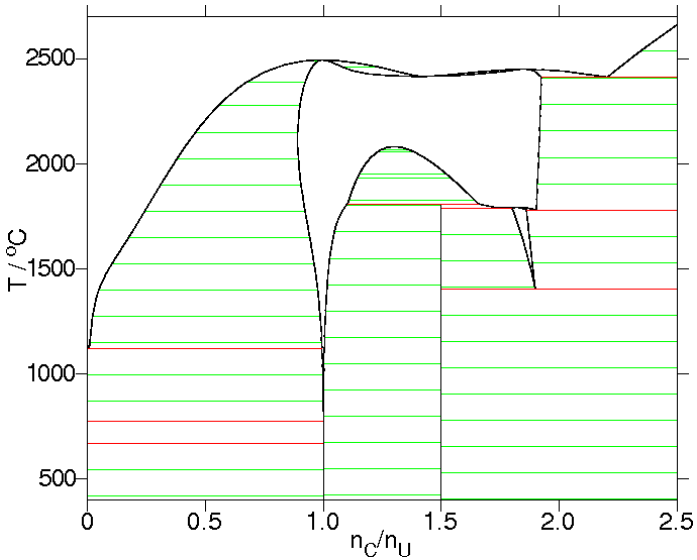
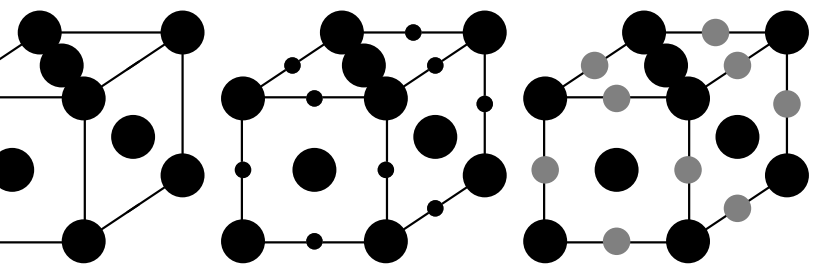
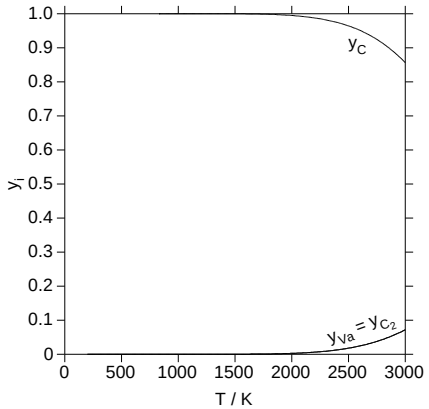
- Be carefull, some disordering or point defects can significantly contribute to the Cp.

Contribution to c_P from point defects

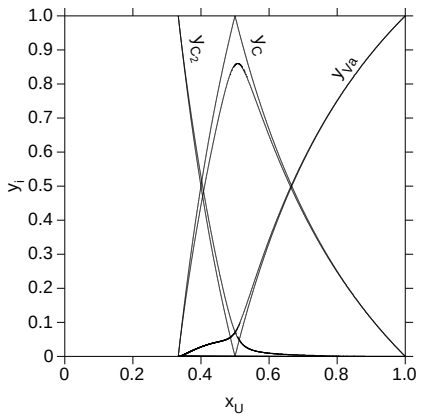
U-C



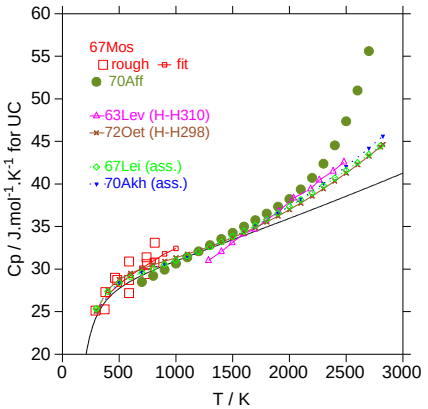




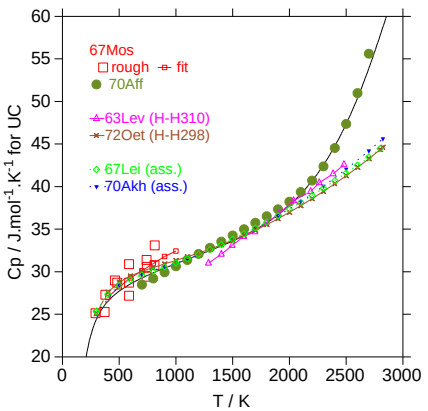
vs temperature for x_C=0.5



vs composition at 1500 and 3000K



(U)(C)



(U)(C,C_2,□) at x_C=0.5

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Compound

When no experimental value is available

- ab initio
- Miedema's estimate
  - original paper
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Avoid to optimise the Gibbs energy of metastable compounds

- ab initio
- $n.100000 + \sum_i n_i \mathrm{GHSER}_i$
- WagnerSchottky equivalence $G_{B:A} = G_{A:A} + G_{B:B} - G_{A:A}$

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- A few extrapolations have been tested in higher order systems.

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- The expertise of the assessor may be key, in particular for systems with little experiments.
- The use of ab initio gives some hopes to overcome these limitations.