“ Fundamentals of Thermodynamic Modelling of Materials ”

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PROFESSOR & TOPIC

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Calcul Thermodynamique - Orcet

*Thermodynamic
Assessments*

[03001]

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Thermodynamic assessments

Nathalie Dupin

Calcul Thermodynamique

November 17, 2010

Outline

- ▶ What is a thermodynamic assessment?
- ▶ Why a thermodynamic assessment?
- ▶ How to performe a thermodynamic assessment?
- ▶ When is it finished?
- ▶ What is the quality/precision of the description?

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.
  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 running a thermodynamic assessment ?

- ▶ This system is a key system for a material, for an application.
- ▶ 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.

How is a thermodynamic assessment used ?

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

How to perform a thermodynamic assessment ?

1. Reading : doing a critical assessment of experimental and theoretical knowledge about the system and the phases.
2. Modelling : defining a model for each phase based on step 1.
3. Optimising : giving 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.

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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How ? Reading

Difficulties to assess uncertainty when scarce data

Al-Co-Cr

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

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

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Experimental techniques

- ▶ phase diagram
  - ▶ metallography (qualitative/quantitative)
  - ▶ 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, chemical potential)
  - ▶ emf (chemical potential, Gibbs energy of formation)
  - ▶ isopiestic (chemical potential)
- ▶ crystallography (X-Ray, neutron, electron diffraction)
  - ▶ identification of the phases
  - ▶ number of sites, multiplicity, occupation $\Rightarrow$ models
  - ▶ site occupancies
  - ▶ molar volumes

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 , $\dots$). The end of 5000+GHSER !
- ▶ volume,
- ▶ ...

Topology of metastable phase diagram

Al-Ni

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Total energy

Nb-Ni

Total energy

Nb-Ni

Prototype μ	Fe ₇ W ₆				
Space group Pearson symbol	<i>R</i> 3̄ <i>m</i> hR13				
Wyckhoff	3a	6c1	6c2	6c3	18h
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

VASP 32 compounds + CEF

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How ? Reading

Total energy

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What is the thermodynamic modelling of a phase?

- ▶ It defines the species contributing to the entropy and to the non-stoichiometry as well as the way these species mix.
- ▶ It defines the general equation of the Gibbs energy
The values of the parameters will be given by least squares method, trial and error or ab initio.
- ▶ It is based on the experimental knowledge of the phase, in particular its crystallography but also the thermodynamic behaviours (H or μ_i vs x or T) or point defects ab initio results.
- ▶ It is better to consider the knowledge of the phase in many different systems 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

- ▶ Modelling the liquid phase in Fe-Ti, the substitutional (Fe,Ti) and the associate (Fe,FeTi,Fe) models induce different equations.
- ▶ Modelling the Laves C14 phase with the CEF (Fe,Ti)₂(Fe,Ti) or (Fe,Ti)₃(Fe,Ti)₂(Fe,Ti) induce different equations.
- ▶ Modelling the A2/B2 or A1/L12 phases with a single equation induces different equations and constraints on the parameters.

Fe-Ti liquid

(Fe,Ti) or (Fe,FeTi,Ti)?

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How ? Modelling

Fe-Ti C14

(Fe,Ti)₂(Fe,Ti) or (Fe,Ti)₃(Fe,Ti)(Fe,Ti)₂ ?

Crystallographie

Prototype MgZn₂ **Strukturbericht** C14 **Pearson** hP12 **Groupe d'espace** P6₃/mmc

Caractéristiques des différents sites pour le prototype

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

- 1 Laves C5
- 2 Ni2ZrB
- 3 Ni2Zr2
- 4 BCC A2
- 5 Laves C4
- 6 Ni10Zr7
- 7 Ni11Zr9
- 8 NiZr
- 9 Ni2Zr2
- 10 LIQUID
- 11 FCC A1
- 12 Ni5Zr

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A2/B2 modelling

A2

B2

L2₁

In order to be able to describe the 2nd order transition between the A2, B2 and L2₁ phases in the ternary system Al-Fe-Ti, the A2 and B2 phases have to be described 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 softwares provide a different way 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 $x^2 = 2 \pm 0.1$ 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 has 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

$$\text{If } L_{A,B}^{\alpha} = a_{A,B}^{\alpha} + b_{A,B}^{\alpha} T$$

$$\Delta H_{mix}^{\alpha} = x_A^{\alpha} x_B^{\alpha} a_{A,B}^{\alpha}$$

- What is the experimental value for ΔH_{mix}^{α} at $x_i^{\alpha} = 0.5$?
- What initial value could be guessed for $a_{A,B}^{\alpha}$?

What initial values?

Substitutional solution

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

What initial values?

Substitutional solution

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

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How ? Optimising

What initial values?

Liquid substitutional solution

When no experimental value is available

Miedema's estimate often provides reasonable starting values:

$$\Delta H \propto -P(\Delta X)^2 + Q(\Delta n_{WS}^{1/3})^2$$

ΔX electronic charge difference of the pure elements

Δn_{WS} difference of the electron densities at the Wigner-Seitz cell boundary

- ▶ original paper
  - ▶ dos ptp by Hari Kumar
  - ▶ windows by Xingqiu Chen (with caution)
- <http://www.tssc.univie.ac.at/xingqiu/xingqiu.html>

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What initial values?

Solid substitutional 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 substitutional 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 $c_p = c_0 + c_1 T + c_{-2} T^{-2} + c_2 T^2 + \dots$

$$\begin{aligned} G_{A_m B_n}^\alpha &= mH_A^{SER_A} - nH_B^{SER_B} \\ &= a + bT - c_0 T \ln T - c_1 T^2 - \frac{1}{2}c_{-2} T^{-1} - \frac{1}{6}c_2 T^3 + \dots \end{aligned}$$

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

Contribution to c_p from point defects

U-C

What initial values?

Compound

When no experimental value is available

- ▶ ab initio
    - ▶ Articles often do not report the total energies needed.
    - ▶ Quantities for reference states may be missing.
    - ▶ Collaboration with experts is recommended.
  - ▶ Miedema's estimate fast but not sensitive to crystal structure
    - ▶ original paper
    - ▶ dos ptp by Hari Kumar
    - ▶ windows by Xingqiu Chen
- <http://www.tssc.univie.ac.at/xingqiu/xingqiu.html>

Avoid to optimise metastable compounds

- ▶ ab initio
- ▶ $n \cdot 100000 + \sum_i n_i \text{GHSER}_i$
- ▶ Wagner-Schottky equivalence

$$G_{B:A} = G_{A:A} + G_{B:B} - G_{A:B}$$

When is it finished?

- ▶ The sum of squares does not decrease any more and you are satisfied. If you are not satisfied,
  - ▶ change uncertainties, weights,
  - ▶ introduce some fictitious equilibria,
  - ▶ use more/less parameters/variables,
  - ▶ modify the model of a phase,
  - ▶ read again available bibliography,
  - ▶ run some experiments.
- ▶ An article or at least a report has been written, figures comparing calculations to experiments have been generated.
- ▶ A few extrapolations have been tested in higher order systems.

What is the quality/precision of the description?

- ▶ It is highly dependent on the amount and quality of the experimental work available.
- ▶ If a good model has been chosen, it is better than a single measurement thanks to the relation imposed between all kind of experimental work taken into account.
- ▶ 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.