Computational Thermodynamics: Learning, Doing and Using

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From Microscopic Understanding to Functionality

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Content

• Introduction
• Basic Thermodynamics
• Thermodynamic Models
• Thermodynamic Databases
• Examples of Applications
• Computer Demonstration
Phase diagrams are visual representations of the state of a material as a function of temperature, pressure, and content of the constituent components.

Binary phase diagrams two dimensions ⇒

Ternary phase diagrams three dimensions, only sections on plane ⇒

More complex systems ⇒ ???
Solution ⇒ the difficulty of graphically representing systems with many components is irrelevant for the CALculation of PHAse Diagrams (CALPHAD) and can be customized for the materials problem of interest.

Computational Thermodynamics - the phase diagram is only a portion of the information that can be obtained from these calculations.
Development of the CALPHAD Method

19th century: Gibbs - correlation between thermodynamics and phase equilibria

1908: van Laar – mathematical synthesis of a binary system

1929: Hildebrand – regular solution concept

1957: Meijering – thermodynamic analysis of Cu-Cr-Ni

1963: Hume-Rothery – phase equilibria in Fe-base alloys

1970: Kaufman and Bernstein – foundation of CALPHAD

1972: Mager – least-squares method for optimization

1973: 1st CALPHAD Meeting

1977: Lukas – first computer software (Lukas Programs)

1977: 1st volume of CALPHAD Journal

1981: Agren, Hillert, Sundman – Compound Energy Formalism

since 1985: continuous development of models and software
Fundamental equations

- Internal Energy  \( U(S,V) \)
- Enthalpy  \( H(S,P) = U + PV \)
- Helmholtz Energy  \( A(T,V) = U - TS \)
- Gibbs Energy  \( G(T,P) = H - TS \)
- Chemical Potential  \( G(T,P,n_i) = \sum n_i \mu_i(T,P) \)
- Gibbs-Duhem eq.  \( \sum n_i d\mu_i = 0 \)
- Activity  \( \mu_i - \mu_i^* = RT\ln a_i \)
Equilibrium condition for isobaric systems (P = const):

\[ G = \sum N_j G_j = \text{minimum} \]

where \( N_j \) is the number of moles, and \( G_j \) is the Gibbs energy of phase \( j \).
Equilibrium condition in a simple binary system

\[ T = 1523 \text{ K} \]

Common tangent construction and calculated phase diagram for the Ni-Cu system
Some definitions

- **Elements** – those from the periodic chart
- **Species** – an element or a combination of elements that forms an entity, like $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{Fe}^{2+}$
- **A phase** is a part of space that has homogeneous composition and structure.
- **Constituents** are the species that exist in a phase.
- **Components** is an irreducible subset of the species
 Thermodynamic models

A model for a phase may contain different species. These species, called the constituents, contribute to the entropy of mixing.

The ideal entropy of mixing:

\[ S = R \ln \left( \frac{? (Ni)!}{(SNi)!} \right) \]

or

\[ S_m = -RSx_i \ln(x_i) \]
**Thermodynamic models**

Pure elements, stoichiometric phases and end-members of solutions:

\[ G = a + bT + cT\ln T + Sd_nT^n \]

Note that the enthalpy, entropy, heat capacity, etc. can be calculated from \( G \):

\[ H = a - cT - S(n-1)d_nT^n \]

\[ S = -b - c - c\ln T - SnT^{n-1} \]

\[ C_p = -c - Sn(n-1)d_nT^{n-1} \]
Thermodynamic models

The Gibbs energy per mole for a solution phase is normally divided into four parts:

\[ G_m = G_m^{rsf} - T S_m^{cfg} + E G_m + G_m^{phys} \]

- \( G_m^{rsf} \) is the reference surface for Gibbs energy
- \( S_m^{cfg} \) is the configurational entropy
- \( E G_m \) is the excess Gibbs energy
- \( G_m^{phys} \) is a physical contribution (e.g., magnetic)
Thermodynamic models

**Ideal solution** (gas, liquid, dilute solid solutions):  
\[ S_{m}^\text{cfg} = -RSx_i \ln(x_i) \]  
\[ \mathcal{E}G_m = 0 \]

**Regular solution:**  
\[ S_{m}^\text{cfg} = -RSx_i \ln(x_i) \]  
\[ \mathcal{E}G_m = H_{\text{mix}} \neq 0 \]

**Subregular solution:**  
\[ S_{m}^\text{cfg} = -RSx_i \ln(x_i) \]  
\[ \mathcal{E}G_m = f(T,x_i) \neq 0 \]

\[ \mathcal{E}G_m = S_i S_{j>i} x_i x_j L_{ij} \]  
\[ L_{ij} = \text{binary interaction parameter} \]

\[ L_{ij} = S_{?} L_{ij}(x_i - x_j)? \] (Redlich-Kister)
Thermodynamic models

Topological features of phase diagrams calculated using regular solution theory (Mager-matrix)
Thermodynamic models

Lattice stability:

$$G_{m}^{rsf}(\text{component } \text{i in phase } \text{j}) - G_{m}^{rsf}(\text{SER})$$

- based on metastable extrapolations
- requires standartization (SGTE)
Thermodynamic models

Compound Energy Formalism (CEF) or sublattice model:
The Gibbs energy expression for \((A,B,...)_a(C,D,...)_c\)

- \(G_{m}^{rsf} = S_i S_j y'_i y''_j \circ G_{ij}\)
- \(S_{m}^{cfg} = -R(a S_i y'_i \ln(y'_i) + c S_j y''_j \ln(y''_j))\)
- \(\circ G_{ij}\) is the Gibbs energy of formation of the end-member compound \(i_a j_c\)
- \(y'_i\) and \(y''_j\) are site fractions
- \(a\) and \(c\) are the site ratios
- The excess and physical contributions are as for a (sub)regular solution on each sublattice.
Thermodynamic models

CEF can be used to describe interstitial solutions, carbides, oxides, intermetallic phases etc. In each particular case, models should be based on the crystallographic information.

- A1 type or Cu type or α-brass, cF4
- A2 type or W type or β-brass, cI2
- B2 type or CsCl type or β-brass, cP2
- A3 type or Mg type or ε, hP2
Thermodynamic models

Excess Gibbs energy in CEF for \((A,B)_a(D,E)_c\)

\[
E_G_m = y'_A y'_B (y''_D L_{A,B:D} + y''_E L_{A,B:E}) + y''_D y''_E (y'_A L_{A:D,E} + y''_B L_{B:D,E}) + y'_A y'_B y''_D y''_E L_{A,B:D,E}
\]

Each L can be a Redlich-Kister series

The surface of reference for the Gibbs energy of a phase \((A,B)_a(D,E)_c\), according to CEF, plotted above the composition square
Thermodynamic models

Associated solution model makes use of fictitious constituents, for example FeS in liquid Fe-S, to describe short range order around the FeS composition.

• A parameter $\delta G_{\text{FeS}}$ is added.

• Interaction parameters between Fe-FeS and FeS-S are added to those between Fe-S $\Rightarrow$ similarity to a ternary system.

• A gas phase is similar to an associated solution (without excess parameters) but in this case the constituents are real.
Thermodynamic models

The ionic liquid model is the modified sublattice model, where the constituents are cations ($M^{q+}$), vacancies ($Va^{q-}$), anions ($X^{p-}$), and neutral species ($B^o$).

- Assumes separate ,,sublattices“ for $M^{q+}$ and $Va^{q-}$, $X^{p-}$, $B^o$, e.g., $(Cu^+)_p(S^{2-}, Va^-, S^o)_Q$, $(Ca^{2+}, Al^{3+})_p(O^{2-}, AIO_{1.5^o})_Q$ or $(Ca^{2+})_p(O^{2-}, SiO_4^{4-}, Va^{2-}, SiO_2^o)_Q$

- The number of ,,sites“ (P, Q) varies with composition to maintain electroneutrality.

- It is possible to handle the whole range of compositions from pure metal to pure non-metal.
The role of magnetism

\[ S_{\text{mag}}(\text{max}) = S_{\text{dis}}(T=\infty) - S_{\text{ord}}(T=0) \]

\[ H_{\text{mag}}(\text{max}) = H_{\text{dis}}(T=\infty) - H_{\text{ord}}(T=0) \]

\[ S_{\text{mag}}(T), H_{\text{mag}}(T) = f(T, T_C, \mu) \]

\[ G_{\text{mag}}(T) = G_{\text{ord}}(T) - G_{\text{dis}}(T) \]

Model for \( G_{\text{mag}}(T) \):

\[ G_{\text{mag}}(T) = RT \ln(\mu + 1) \ g(\tau) \quad \tau = T/T_C \]

\[ g(T) = 1 - K_1(\tau^{-1} + K_2(\tau^3/6 + \tau^9/135 + \tau^{15}/600) \quad \tau < 1 \]

\[ g(T) = -K_3(\tau^{-5}/10 + \tau^{-15}/315 + \tau^{-25}/1500) \quad \tau > 1 \]
Flowchart of the CALPHAD method

- Theory
  - Quantum Mechanics
  - Statistical Thermodynamics

- Estimates
  - Models with adjustable Parameters
  - Adjusting the Parameters
  - Thermodynamic Functions $G, H, S, C_P = f(T, P, x, ...)$

- Experiments
  - DTA, Calorimetry, EMF, Vapor pressure
  - Metallography, X-Ray diffraction, ...

- Thermodynamic Optimization
  - Ab-initio calculation

- Storage
  - Databases, Publications

- Equilibrium Calculations
  - Phase Diagrams

- Applications

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Connection with first-principle calculations

- From first principles one may calculate the energy at 0 K for different configurations of atoms on specific lattices.

- The cluster energies can then be used in a Cluster Variation Method calculation of the phase diagram for example.

- The cluster energies can also be used for Monte-Carlo simulations of the phase diagram.

- The energies from a first principle calculation can also be used directly in a sublattice model if the configurations correspond to the compounds.
Experimental data

1. Crystallographic data
2. Phase Diagram data
3. Thermochemical data
4. Physical property data
Crystallographic data

- Structure of the phases in the system.
- Sublattices for different constituents.
- Types of defects for non-stoichiometric compounds.

A1  B1  L1\textsubscript{0}  L1\textsubscript{2}  A2  B2  D0\textsubscript{3}  L2\textsubscript{1}
Phase diagram data

- **Thermal analysis**: start/end temperatures of transformations
- **Microscope**: phase identification, determining phase amounts
- **X-ray**: phase identification, lattice parameters
- **Microprobe**: phase identification, phase compositions (tie-lines)
- **X-ray and neutron diffraction**: site occupancies
Thermochemical data

- Calorimetric data: enthalpy of formation, ~ of transformation, ~ of mixing
- EMF, Knudsen cell data: chemical potentials, activities
- Partial pressure: activities
- DSC: heat content, heat capacity, enthalpy of transformation
Model selection

- Special behaviour of data, like strong "V" shaped enthalpy of mixing (sharp raise of activity).
  - solid phase = long range order
  - liquid phase = short range order
- Same phase may occur in several places in the system (or related phases like ordered superstructures).
Thermochemical properties for Fe-S

The phase diagram and some thermodynamic properties: activity, enthalpy and entropy at 2000 K

Modeling of the liquid phase

metallic systems: sub(regular) solution model

metal-nonmetal systems: associated or ionic liquid model.
Numerical method for assessment

- The basic fitting is to vary the model parameters to minimize the difference between the experimental value \( q_i^{\text{exp}} \) and the same quantity calculated \( q_i^{\text{calc}} \) from the model.

- \[ \text{Err} = S_i \left( \frac{(q_i^{\text{exp}} - q_i^{\text{calc}}) w_i}{s_i} \right)^2 \]

  \( w_i \) is a weight assigned to the experimental value

  \( s_i \) is an experimental error (standard deviation)
Higher component systems

\[ E_G^m = S_i S_{j>i} x_i x_j L_{ij} + x_i x_j x_k L_{ijk} \]

\[ L_{ijk} = v_i^0 L_{ijk} + v_j^1 L_{ijk} + v_k^2 L_{ijk} \]

\[ v_i = x_i + (1 - x_i - x_j - x_k)/3 \]

In the ternary system \( v_i = x_i \)

In higher order systems \( S_i v_i = 1 \) that guarantees the symmetry

\( L_{ijk} \) is a ternary interaction parameter

Higher order interaction parameters can be usually omitted (a few exceptions in quaternary systems)
Examples of applications

• Ni-Al based intermetallic alloys
• Micro-alloyed steels
• Oxide inclusions in steels
• Solders
• Simulation of microstructure
Ni-Al based intermetallic alloys

(a) Isothermal Section at T=1300°C

(b) Ni-25Al-XFe Vertical Section

a) Ni-25Al-18Fe; b) -15Fe; c) -13Fe

(a) L1$_0$ Martensite $\rightarrow$ B2 $\rightarrow$ $\beta + \gamma'$ (widman.)

(b) L1$_0$ Martensite $\rightarrow$ Ni3Al $\rightarrow$ $\gamma' + \beta$ $\rightarrow$ $\beta + \gamma'$ (lam.-type I)

(c) L1$_0$ Martensite $\rightarrow$ Ni3Al $\rightarrow$ $\beta + \gamma'$ (lam.-type II) $\rightarrow$ $\beta + \gamma'$ (blocky)

Room Temp. $\rightarrow$ 300°C $\rightarrow$ 700°C $\rightarrow$ 800°C Heating Temperature
Micro-alloyed steels (HSLA)

Projected miscibility gap for the case of (Ti,Nb)(C,N)

Calculated percentage of phases in microalloyed steels showing precipitation of TiN- and NbC-based carbides
Oxide inclusions in steels

Calculated isothermal sections CaO-FeO-SiO$_2$ (a) and CaO-MgO-SiO$_2$ (b)

Calculated phase fractions vs temperature for two different compositions

Calculated liquidus surface for five-component oxide system with fixed contents of Al$_2$O$_3$ and MgO
Solders (Ag-Bi-Sn)

a) Liquidus surface; b) solidus surface

Scheil Calculations

Sn + Ag₃Sn begins

Ternary Eutectic

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Simulation of microstructure

Thermo-Calc

TQ-interface

relinearisation

thermodynamic database

thermodynamic description

\( \Delta G, c^\alpha, c^\beta \)

PF-solver

temp.-solver

conc.-solver

output

time-loop

MICRESS

results
Solidification of Al-4.8at%Ag-16.0%Cu

Evolution of the liquid composition according to simulation

Liquidus projection in the Al-rich corner of Al-Cu-Ag
7-Component dendritic superalloy IN706

2D-Simulation using a moving frame:

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>bal</td>
<td>37.7</td>
<td>17.1</td>
<td>1.83</td>
<td>1.8</td>
<td>0.55</td>
<td>0.05</td>
</tr>
</tbody>
</table>
**Solidification of IN706 using the unit cell model**

- **PF-method**
- **Scheil**

\[ (dT/dt = -0.5 \text{ K/s}, \lambda = 200 \text{ µm}) \]

- **Images:**
  - Image 1: Material distribution pattern
  - Image 2: Material distribution pattern
  - Image 3: Material distribution pattern
  - Image 4: Material distribution pattern

**Graph:**
- **Y-axis:** \( f_{\text{Liq}} \)
- **X-axis:** \( T/\degree C \)
- **Points:**
  - 1100
  - 1200
  - 1300
  - 1400

**Colors:**
- **Color Bar:**
  - Range: 0.02 to 0.12
  - Scale: 0.02, 0.04, 0.06, 0.08, 0.10, 0.12

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Microstructure after solidification

[Image of a microstructure diagram showing elements Al, C, Cr, Fe, Nb, Ti with annotations for MC, η, and Laves phases.]