

Computer Calculations of Equilibria and Phase Diagrams

Bo Sundman

Understanding thermodynamic models
and using them to determine model
parameters to fit theoretical and
experimental data

Plan for concentrated course

- 4 lectures, 2 each week.
- Homework, if well done course ready.
- Written or oral completion if some homework not up to requirement.
- 3 graduate points.
- Software and manuals can be downloaded from <http://www.thermocalc.se>

Schedule for seminar room

- Monday 16/10 at 13-15
- Thursday 19/10 at 13-15
- Monday 23/10 at 13-15
- Thursday 26/10 at 13-15

Lectures

- 1: Thermodynamics: Equation of State, Gibbs energy. Regular solution, sublattice model, lattice stabilities, enthalpy models, entropy models, associate models, quasichemical models, CVM, configurational terms, Monte Carlo. Numerical methods for equilibrium calculation
- Articles: Bo J TRITA, Mats CEF, dilute solutions
- Homework: using TC binary module. Running TC example 2 and some TC multicomponent examples. Selecting an individual system for assessment, oxide demo program

- 2: Experimental and theoretical information, crystallography, enthalpies, activities, phase diagram, using *ab initio*. Criteria for selection of models for phases in a system. Numerical methods for assessment. Assessment of binary systems. Use of PARROT. The alternate mode. Kaufman/Ansara assessment method calculating metastable regions. Decision on an individual system to assess.
- Articles: Chapter 7.2 from book and some assessment papers
- Homework: TC example 36, testing different strategies.

- 3: Creating the experimental data file. Modelling intermetallics like sigma, mu and phases with order/disorder transformations like A2/B2, A1/L1₂/L1₀. Partitioning the Gibbs energy. Creating databases from assessments, extrapolations to multicomponent systems.
- Articles: Re-W paper, Ringberg paper.
- Homework: TC example 31, Assessment of Co-V

- 4: Strategies to find reasonable set of parameters. Modelling liquids: ionic liquid, molten salts, aqueous etc. Models for solid metal-nonmetal systems: carbides, nitrides, oxides etc.
- Articles: 84Hil, ionic liquid, some associated model paper, some assessment papers
- Homework: Assessment of an individual system selected earlier

Thermodynamics

- Equation of state, for example ideal gas
 $pV = nRT$
- Equation of state is not suitable for modelling of composition dependence.
- The ideal gas equation can be integrated to a Gibbs energy: $G = nRT \ln(p/p_0)$

Thermodynamics

- Fundamental equations (unary systems)
- $U(S,V)$ Internal energy
- $H(S,p) = U + pV$ Entalpy
- $A(T,V) = U - TS$ Helmholtz energy
- $G(T,p) = U + pV - TS$ Gibbs energy

Thermodynamics

A multicomponent system consists of many different *species* (molecules). There are reactions among these, like $2\text{CO} + \text{O}_2 = 2\text{CO}_2$

The *components* are an irreducible set of the species.

The fraction of components are independent but not the fraction of species.

Thermodynamics

- Fundamental equations (multi-component).
 N_i is moles of component i , y_j is constituent fraction of species j
- $G(T,p,N_i) = \sum_i N_i \mu_i(T,p,y_j)$
- $dG = \sum_i \mu_i dN_i$
- $0 = \sum_i N_i d\mu_i$ Gibbs-Duhem
- $G(T,p,N_i) = \sum_\varphi N^\varphi G_m^\varphi(T,p,y_j)$

Change of components

- When changing to a new set of components the chemical potentials of the new set i is related to the original set j by
- $\mu_i = \sum_j b_j \mu_j$
- where b_j are the stoichiometric factors

Thermodynamics

- A phase is a part of space that has homogeneous composition and structure.
- The term phase can be extended to non-equilibrium cases when the structure and the composition may vary continuously from one place to another.
- The term phase will also be used just for a structure, with arbitrary components.
- The term phase will also be used for the gas, liquid and amorphous phases which have no structure.

Thermodynamics

- A homogeneous reaction between species means that the reaction takes place inside a phase, for example $2\text{H}_2\langle\text{g}\rangle + \text{O}_2\langle\text{g}\rangle = 2\text{H}_2\text{O}\langle\text{g}\rangle$
- A heterogeneous reaction means that two or more phases are involved, for example $\text{O}_2\langle\text{g}\rangle + \text{C}\langle\text{s}\rangle = \text{CO}_2\langle\text{g}\rangle$
- Some of the problem in understanding thermodynamics is due to the fact that often no distinction is made between these reactions.

Thermodynamic models

- A model for a phase may contain real and fictitious species. These species, called the *constituents*, contribute to the entropy of mixing.
- The ideal entropy of mixing of a phase having the components as constituents comes from Boltzmann $S = R \ln(\Pi(N_i)! / (\Sigma N_i)!)$
- This can be derived in two ways, either distributing different atoms on a given set of lattice points or from the statistical mechanics of an ideal gas.

Thermodynamic models

- From Stirling's formula per mole of phase $S_m = -R \sum_i x_i \ln(x_i)$
- Mole fraction of components, $x_i = N_i / \Sigma N_i$
- Constituent fraction, y_i , is equal to the amount of the constituent divided by the total amount of constituents on a lattice. For a gas phase each molecule has a constituent fraction.

Thermodynamic models

- **Elements** – those from the periodic chart
- **Species** – an element or a combination of elements that forms an entity, like H₂O, CO₂, Fe⁺²
- **Constituents** are the species that exist in a phase. A constituent can be real or fictitious.
- **Components** is an irreducible subset of the species

Thermodynamic models

- Each phase is modelled separately
- Phases with no compositional variation has just an expression $G(T,p)$. That is very simple to handle at low pressures.
- Phases with a small compositional variation can be very difficult to model as one should take into account the different types of defects that cause the non-stoichiometry

Thermodynamic models

- The temperature dependence of a Gibbs energy parameter is normally a polynomial in T, including a $T \ln T$ term from the heat capacity
- $G = a + bT + cT \ln T + dT^2 + \dots$
- Note that the enthalpy, entropy, heat capacity etc can be calculated from this G.
- The pressure dependence, except for a pressure independent volume, is more complicated and will be discussed later

Thermodynamic model

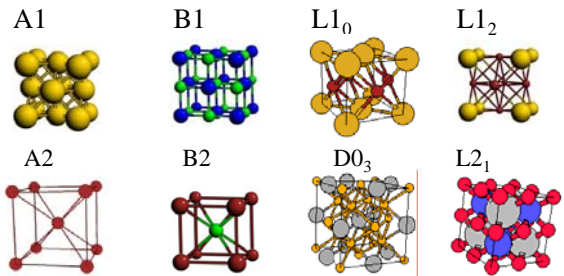
- Properties at low temperature, normally below 300 K, is normally not modelled.
- The Gibbs energy at low temperature has a complicated T-dependence (Debye model) that is not easy to combine with the higher temperature properties.
- Enthalpy data at 0 K, from *ab initio* calculations, are useful for fitting high temperature data

Thermodynamic models

- Phases with extensive compositional variation are the gas and liquid or have usually rather simple lattices for example fcc (A1), bcc (A2) and hcp (A3).
- Some more complex lattices belong to families of simpler lattices, like B1 is A1 with interstitials, B2 is ordered A2 etc. That should be taken into account in the modelling

Crystallographic data

<http://cst-www.nrl.navy.mil/lattice/>



Thermodynamic models

- From the thermodynamic models one can calculate various thermodynamic properties of a system, like heat of transformation, chemical potentials, heat capacities etc
- One may also calculate the phase diagram or metastable extrapolations of the phase diagram
- **One may make more reliable extrapolations in temperature and composition than if one extrapolated a single property**
- **They can be used in software for simulations of phase transformations**

Thermodynamic models

- The Gibbs energy per mole for a solution phase is normally divided into four parts
- $G_m = {}^{srf}G_m - T {}^{cfg}S_m + {}^E G_m + {}^{phys}G_m$
- ${}^{srf}G_m$ is the surface of reference for Gibbs energy
- ${}^{cfg}S_m$ is the configurational entropy
- ${}^E G_m$ is the excess Gibbs energy
- ${}^{phys}G_m$ is a physical contribution (magnetic)

Thermodynamic models

Modelling by physicists have mainly concentrated on finding a good configurational entropy (Quasichemical, CVM, Monte Carlo) to describe main features or a specific detail.

Modelling among material scientists has mainly concentrated on finding a good excess Gibbs energy to reproduce the experimental data.

Regular solutions

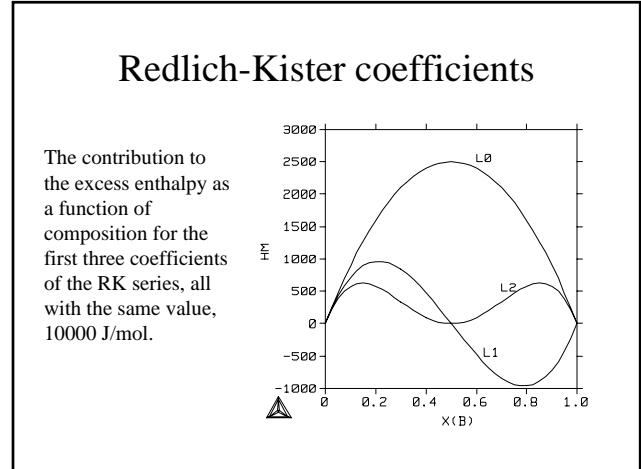
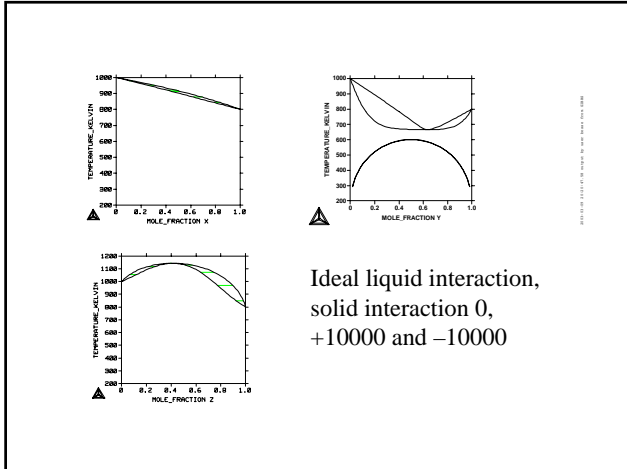
- Regular solution models are based on ideal entropy of mixing of the *constituents*. In the general case these are different from the *components* and their fraction is denoted y_i
- $G_m^\phi = \sum_i y_i {}^\circ G_i^\phi + RT \sum_i y_i \ln(y_i) + {}^E G_m^\phi$
- ${}^\circ G_i^\phi$ is the Gibbs energy of pure constituent i in phase ϕ
- ${}^E G_m$ is the excess Gibbs energy

Excess energies

- If A and B atoms occupy neighbouring lattice sites the energy of the AB bond is related to that of an AA and a BB bond by
- $E_{AB} = \epsilon_{AB} - 0.5 (\epsilon_{AA} + \epsilon_{BB})$
- If this energy is negative the atoms like to surround themselves with the other kind of atom.
- If the energy is positive there is a demixing

Regular solution model

- The excess Gibbs energy for a binary system
- ${}^E G_m = \sum_i \sum_{j>i} y_i y_j L_{ij}$
- $L_{ij} = \sum_v (y_i - y_j)^v {}^v L_{ij}$ (Redlich-Kister)
- Other types of polynomial are possible but all are identical in the binary case. However, they will differ in ternary extrapolations and thus the most symmetrical is preferred
- $L_{ij} = 0.5 z E_{ij}$ where z is the number of nearest neighbours.



Ternary regular solution parameter

- $E_{G_m} = y_i y_j y_k L_{ijk}$
- $L_{ijk} = v_i {}^0L_{ijk} + v_j {}^1L_{ijk} + v_k {}^2L_{ijk}$
- $v_i = y_i + (1 - y_i - y_j - y_k)/3$

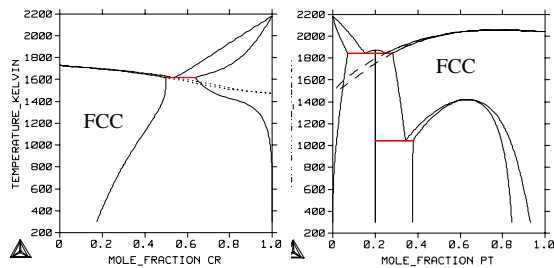
In the ternary system $v_i = y_i$. In higher order systems $\sum v_i = 1$ always which guarantees the symmetry.

Lattice stabilities

A solution model for a phase often extend from one pure component to another even if one, or both, of them may not exist as stable in that phase.

These "lattice stabilities" of the metastable states of elements was first introduced by Larry Kaufman and must be agreed internationally to make assessments compatible. Most commonly used are those by SGTE, published in Calphad by Dinsdale 1991

Liquidus extrapolations for Cr



Lattice stability for Cr

First principle calculations have shown fcc-Cr is mechanically unstable, thus it is impossible to calculate the energy difference between fcc and bcc for pure Cr.

It has been accepted that the "Calphad" value is reasonable within the range Cr dissolves in a stable fcc phase and as long as one does not believe it represents a real fcc phase.

Dilute solution model

- Based on Henry's law for the activity of the solute and Raoult's law for the activity of the solvent. "Epsilon" parameters describe the activity in more concentrated solutions.
- The assumption that Raoult's law is true for multicomponent systems is wrong
- Dilute models are thermodynamically inconsistent (they do not obey the Gibbs-Duhem equation) and cannot be used in software for Gibbs energy minimizations.

Sublattice model

Crystalline phases with different types of sublattices for the constituents can be described with the sublattice model. Different constituents may enter in the different sublattices and one assumes ideal entropy of mixing on each sublattice. The simplest case is the reciprocal system $(A,B)_a(C,D)_c$

Sublattice model

- The Gibbs energy expression for $(A,B)_a(C,D)_c$
- $^{srf}G_m = \sum_i \sum_j y'_i y''_j {}^oG_{ij}$
- $^{cfg}S_m = -R(a \sum_i y'_i \ln(y'_i) + c \sum_j y''_j \ln(y''_j))$
- ${}^oG_{ij}$ is the Gibbs energy of formation of the compound $i_a j_c$, also called “end members”.
- a and c are the site ratios
- The excess and physical contributions are as for a regular solution on each sublattice.

Sublattice model

Excess Gibbs energy for $(A,B)_a(C,D)_c$

$${}^E G_m = y'_A y'_B (y''_C L_{A,B:C} + y''_D L_{A,B:D}) + y''_C y''_D (y'_A L_{A:C,D} + y'_B L_{B:C,D}) + y'_A y'_B y''_C y''_D L_{A,B:C,D}$$

Each L can be a Redlich-Kister series

Sublattice model

- The sublattice model has been used extensively to describe interstitial solutions, carbides, oxides, intermetallic phases etc.
- It is often called the compound energy formalism (CEF) as one of its features is the assumption that the compound energies are independent of composition and it includes several models as special cases.
- Note that the G_m for sublattice phases is usually expressed in moles for formula units, not moles of atoms as vacancies may be constituents.

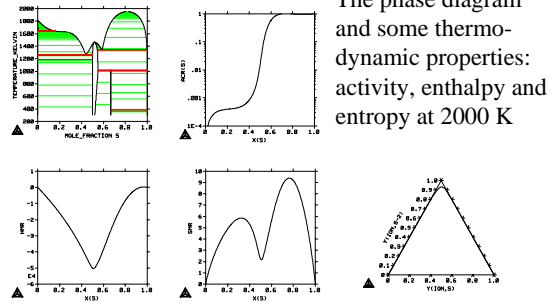
Sublattice model

- Sublattices are used to describe long range order (lro) when the atoms are regularly arranged on sublattices over large distances.
- Short range order (sro) means that the fraction of atoms in the neighbourhood of an atom deviate from the overall composition. There are special models for that.

Associated solutions

- These are identical to regular solutions except that one has added one or more fictitious constituents, for example FeS in liquid Fe-S. The reason to introduce this is to describe short range order around the FeS composition.
- A parameter ${}^{\circ}G_{\text{FeS}}$ describe the stability of the associate.
- Interaction parameters between Fe-FeS and FeS-S are added to those between Fe-S. It can thus be modelled similarly to a ternary system.
- Note that a gas phase is similar to an associated solution (without excess parameters) but in this case the constituents are real.

Thermochemical properties for Fe-S



Quasichemical model

- Quasichemical models are derived using mixing the fractions of bonds y_{AA} , y_{AB} and y_{BB} rather than constituents y_A and y_B . But one may also treat this as a model with the additional constituents AB and BA and a quasichemical configurational entropy.
- $$S_m = -Rz/2 (y_{AA} \ln(y_{AA}/y_A y_A) + y_{AB} \ln(y_{AB}/y_A y_B) + y_{BA} \ln(y_{BA}/y_B y_A) + y_{BB} \ln(y_{BB}/y_B y_B)) - R(y_A \ln(y_A) + y_B \ln(y_B))$$

Quasichemical model

- There is a reason to have both AB and BA bonds as in a lattice this is related to the constituents to the left or right of the bond. The fraction of the constituents can be calculated from the "bond" fractions

$$y'_A = 0.5(y_{AA} + y_{AB}) \quad y'_B = 0.5(y_{BA} + y_{BB})$$

$$y''_A = 0.5(y_{AA} + y_{BA}) \quad y''_B = 0.5(y_{AB} + y_{BB})$$

- It is possible to include long range order in the quasichemical model by allowing y'_A and y''_A to be different, i.e. y_{AB} not equal to y_{BA} . This is similar to a lro model (A,B)(A,B)

Quasichemical model

- The degree of short range order, ϵ , can be evaluated from the difference between the "fraction of bonds" and the product of the constituent fractions

$$y_{AA} = y'_A y''_A - \epsilon$$

$$y_{AB} = y'_A y''_B + \epsilon$$

$$y_{BA} = y'_B y''_A + \epsilon$$

$$y_{BB} = y'_B y''_B - \epsilon$$

Cluster Variation Method

- An improved method to treat short range order in crystalline solids was developed 1951 by Kikuchi and called Cluster Variation Method (CVM). It can treat arbitrarily large clusters of lattice sites but the entropy expression must be derived for each lattice.
- Even for binary systems it can be rather cumbersome to use CVM and for multi-component systems it is impossible to apply. Anyway, for most multicomponent phases the contribution to Gibbs energy due to sro is small.

Comparisons CVM-Associated-Sublattice

- A model describing short range order should have ideal entropy of mixing when the pair energy ${}^0G_{AB}$ is zero. That is the case for the quasichemical model but not for the associated model. A reason that the associated model is still used is that it is simpler to handle.
- The relation between the quasichemical model and the sublattice model can be extended to the CVM. A disadvantage with the sublattice model is that it does not include sro but it is easier to handle than CVM.

Numerical consideration

The Gibbs energy models should be expressed using the independent constituent variables of the phase. In some software the mole fraction is used as independent composition variable globally and the constituent fractions (bonds, associates, molecules) of each phase is minimized separately. This is a disadvantage as the minimization of the Gibbs energy to find the equilibrium can be made faster for the independent constituents of the phase and that no separate minimization of bond fractions or clusters is needed.

Numerical consideration

Thermo-Calc uses Gibbs energy minimization with Lagrangian multipliers. This requires first and second derivatives of the Gibbs energy to have fast and stable convergence. These derivatives are calculated analytically which require more code but gives faster execution.

Although the calculation of second derivatives is not absolutely necessary it has the extra benefit that these second derivatives are used in the thermodynamic factor for the diffusion coefficients and can thus be used also to speed up simulations.

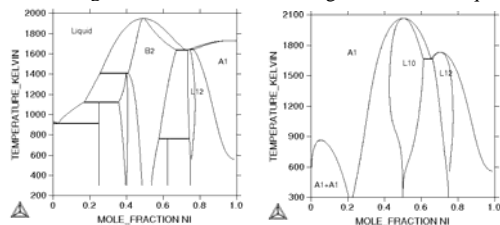
Connection with first principle calculations

From first principles one may calculate the energy at 0 K for different configurations of atoms on specific lattices. These energies can be expanded in different ways to describe disordered states for compositions in between the calculated configurations. A popular model to use is the Cluster Expansion Method (CEM) by Connally-Williams. The cluster energies can then be used in a CVM or Monte Carlo (MC) calculation of the phase diagram for example.

For phase diagram calculations of ordering in binary systems with fcc lattices it is very important to include the short range order but for carbides and intermetallic phases like σ it is less important.

Connections with first principle calculations

The energies from a first principle calculation can also be used directly in a sublattice model if the configurations correspond to the end members. For fcc there are theoretically 3 ordered compounds, two with $L1_2$ and one with $L1_0$ structure. But like in the Al-Ni system below some may be metastable and their energies must be calculated using *ab initio* techniques.



Articles

- TRITA-MAC about POLY and PARROT
- Description of CEF
- Relation between the dilute solution model and the regular solution model

Homework

- Calculate a number of binary systems using the BIN module. Select one system and plot the phase diagram in various ways. Calculate also G curves and other properties and discuss the relations with the phase diagram.
- Follow TCEX02 and discuss the various calculations and diagrams.
- Follow TCEX19 and comment on the calculations.
- Select a binary system you want to assess. It may be an already assessed system.

End of lecture

- See you on Thursday, same time in B2