Computer Calculation of Equilibria and Phase Diagrams

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2nd lecture

Homework

- Problems to download or run TCC?
- Running the BIN module?
- Running the examples?
- Oxide demo?

- 2. Experimental and theoretical information, crystallography, enthapies, 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 6.2 from book and some model papers
- Homework: TC example 36, testing different strategies.

Data for assessments

- Theoretical information
- Experimental data
- Estimated data
- Assessments of similar systems

Theoretical information

- Thermodynamic relations.
- Stability conditions
- First principle calculations of enthalpies of formation of given compounds.

Experimental data

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

Crystallographic data

- Find the structure of the phases in the system. Determine sublattices for different constituents. Note that the space groups or Pearson numbers does not uniquely define a lattice. For example FCC and $D0_3$ have the same space group.
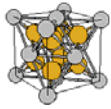- Types of defects for non-stoichiometric compounds.

Crystallographic data

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

A1   B1 $L1_0$ $L1_2$

A2   B2 $D0_3$ $L2_1$
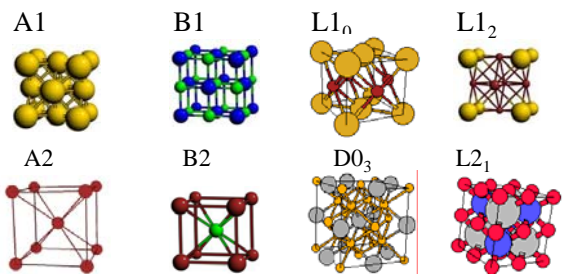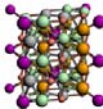
Crystallographic data

C1 $D0_{22}$ $D8_b$ (σ)

Crystallographic data

- Sublattices are specified when the phase is entered in the Gibbs Energy System (G-E-S)

ENTER-PHASE

Name: BCC_A2

Type:

Number of sublattices /1/:2

Number of sites on sublattice 1/1.0/: 1.0

Number of sites on sublattice 2/1.0/: 3.0

Crystallographic data

- In many cases the crystallographic data must be simplified before used in a thermodynamic model. Thus the σ phase is modelled with 3 sublattices and not 5 and all elements are not entered in all sublattices.
- Many intermediate phases have little or no crystallographic information. One may then use the stoichiometric formula.

Crystallographic data

- Phases with order/disorder transformations will be discussed later. Sublattices for chemical ordering are entered as for interstitial sublattices or carbides, but the constituents and energy parameters have specific relations.

Parameter notation

A parameter is denoted

<symbol>(<phase>, <constituent array>;<degree>)
 <function of T and p>

G(liquid,Fe;0), L(liquid,Al,Fe;0), L(fcc,Fe:C,Va;0)

<symbol> can be G or L for energy parameters,
   TC for magnetic transition temperaure,
   V0 for the volume at 298.15 and 1 bar etc.

Parameter notation (cont.)

- A constituent array has at least one constituent in each sublattice. These constituents in different sublattices are separated by colon ":".
- An interaction parameter has two or more constituents in one or more sublattices. The constituents in the same sublattice are separated by a comma ",".
- An interaction parameter may have a "degree" and the meaning of this depend on the excess model of the phase. Default degree is zero.

Parameter notation (cont.)

- The <function> is written with a <low T limit>, <expression terminated with semicolon ";">, <high T limit> followed by a Y or N if there is an expression above the high T limit.
- Example: Gibbs energy of pure FCC Cr
  G(FCC,Cr) 298.15 GHSERCR+7284+0.163*T; 6000 N
- GHSERCR is the name of a function that describes the properties of pure BCC Cr and is entered separately and can be used for several parameters.

Parameter notation

- The vacancy, Va, is a possible constituent in a sublattice. Interstitial sublattices are normally mainly vacant i.e. filled with vacancies. Note that parameters are for a formula unit of a phase. Thus G(FCC,Fe:Va) is for one mole of Fe and G(FCC,Ti:C) is for two moles of atoms, one Ti and one C.
- Example of interaction parameters are
  L(FCC,Fe,Cr:Va;0) 298.15 10833-7.48*T; 6000 N
 L(FCC,Fe,Cr:Va;1) 298.15 1410; 6000 N

Physical property data

- Magnetic phases have a Curie temperature and Bohr magneton number that are composition dependent. The magnetic contribution is calculated as
- $G_m^{magn} = RT\, f(\tau)\, \ln(\beta+1)$
- $\tau = T/TC$. TC and β are composition dependent.
- The function $f(\tau)$ is empirical.

Physical property data

- Magnetic phases are specified with the AMEND-PHASE-DESCRIPTION command in G-E-S. This command requires the "anti-ferromagnetic factor" and the fraction of magnetic enthalpy above the Curie temperature. For FCC phases these are –3 and 0.28, for BCC they are –1 and 0.4
- Note that magnetic transitions at low temperatures may be ignored as the paramagnetic state at high temperature is the reference state.

Physical property data
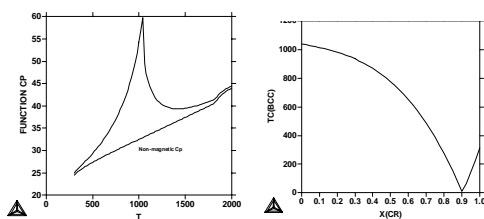
Physical property data

- There are new parameters to describe the volume of the phase
- V0(phase, constituent array) is the volume at 298.15 K and 1 bar
- VA(phase, constituent array) is the integrated thermal expansivity at 1 bar.
- Both of these can be composition dependent

Thermochemical data

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

Thermochemical data

- Enthalpy of mixing in the liquid is very useful. Unfortunately almost no one is measuring this any more. A theoretical technique to estimate this would be very helpful.

Phase Diagram data

- DTA: start/end temperatures of transformations
- Microscope: phase identification, determining phase amounts
- X-ray: phase identification, lattice parameters
- Microsond: phase identification, phase compositions (tie-lines)
- Neutron diffraction: site occupancies

Estimation of missing data

Missing data that are essential for a good assessment can be estimated in various ways:

- Comparisons with similar systems
- Calculations using first principles
- Miedema or similar estimation formulae

Use of data from similar systems

- Use same models for the same phases.
- Extract experimental data missing from own system

The POP file

- Experiments are described like an equilibrium calculation in POLY. Additional information provided as EXPERIMENT or as SET-ALTERNATE-COND. LABEL and GRAPHICAL are useful during optimization.

CREATE-NEW 5 1
CHANGE-STATUS PHASE FCC LIQ=FIX 1
SET-COND T=1000 P=1E5
LABEL AFL
EXPERIMENT X(LIQ,CR)=0.22:0.02
SET-ALTERNATE-COND X(FCC,CR)=0.18
GRAPHICAL 1 0.22 1000 4
COMMENT From Acta Met ?????

The POP file

- Experiments are described independently of the models used for the phases.
- All kinds of experiments can be used in the same POP file.
- Use raw data, not polished or fitted. Never read data from a hand-drawn phase diagram.
- Use GRAPHICAL to plot experimental data from the POP file, SET-ALTERNATE-COND to help with start values, LABEL to handle weights.

The POP file

- Tables in POP files require only one description of the equilibrium, the same is repeated for each line in table

TABLE-HEAD 100
CREATE-NEW @@ 1
CHANGE-STATUS PHASE @1 @2 =FIX 1
SET-COND T=@3 P=1E5
EXPERIMENT X(@1,CR)=@4:5% X(@2,CR)=@5:10%
LABEL @6
TABLE-VALUES
FCC LIQ 1000 0.18 0.22 AFL
**BCC LIQ 1100 0.16 0.20 ABL**
…

The POP file

- Thermochemical data can also be used for example this showing an enthalpy of mixing in the liquid

```
CREATE-NEW 200 1
CHANGE-STATUS LIQ=FIX 1
SET-REFERENCE-STATE CR LIQ * 1E5
SET-REFERENCE-STATE FE LIQ * 1E5
SET-COND T=2000 P=1E5 X(CR)=.15
EXPERIMENT HMR=-4500:500
```
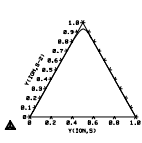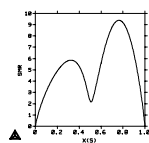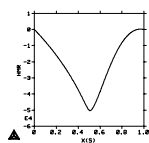
Model selection

- Special behaviour of data, like strong "V" shaped enthalpy of mixing (sharp raise of activity). In a crystalline phase this indicates long range order, in a liquid short range order.
- Same phase may occur in several places in the system (or related phases like ordered super-structures)
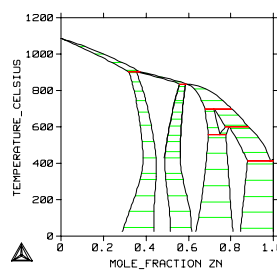- Use same models as in previous assessments of the same phase.

Thermochemical properties for Fe-S
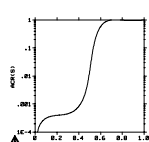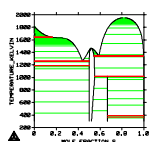
The phase diagram and some thermo-dynamic properties: activity, enthalpy and entropy at 2000 K

Cu-Zn, several BCC phases

Model selection

- The **liquid phase** in metallic systems is most often modelled with a substitutional regular solution model.
- For metal-nonmetal systems with strongly assymetric miscibility gaps or rapid change of activities this is often not good and an *associated, quasichemical* or *ionic liquid* model may be used instead. These will be described later.
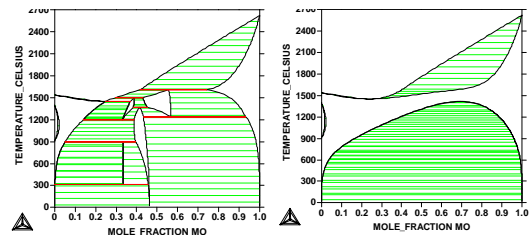
Model selection

- The **terminal phases** are those for the pure elements, "end-members". Usually the properties of these are known for both components (lattice stabilities). One must not change these lattice stabilities without a very good reason.
- The mixing in a terminal phase may be substitutional or interstitial.
- Sublattice phases may have different mixing on each sublattice.

Model selection

- Some terminal phases may extend far into the system and this makes it possible to determine the excess Gibbs energy accurately. But often the solubility is very low and one must use few excess parameters.
- In some cases one may have the same terminal phase on both sides but one or more intermediate phases in between. But the terminal phase must be modelled as the same phase.

The Fe-Mo with and without intermediate phases

Model selection

- An **intermediate phase** is any phase which does not extend to the pure elements (or end-members).
- The name **intermediate** is preferred to **intermetallic** as it can also be used for carbides and oxides.
- An intermediate phase can have extensive solubility and a simple lattice like BCC or FCC but often it has restricted solubility and sometimes the structure is unkown. Most often they have at least two sublattices with different constituents. The Compound Energy Formalism (CEF) can often provide a reasonable model.

Phases with order/disorder transformations

- Some intermediate phases represent ordered BCC, FCC and HCP lattices. There are a number of established techniques to model phases with order/disorder as the ordered phases should become identical to the disordered phase when the ordering is no longer stable. This is achieved by partitioning the Gibbs energy in two parts
- $G_m = G_m^{dis} + \Delta G_m^{ord}$

ΔG_m^{ord} is zero when the phase is disordered

Order/disorder

- A2/B2 ordering in BCC is modelled with two sublattices, sometimes also with a third for interstitials. $(Fe,Al,Ni)_{0.5}(Fe,Al,Ni)_{0.5}(Va,C)_3$
- B2 ordering require G(B2,Fe:Al)=G(B2,Al:Fe) as the two sublattices are identical. The interaction parameters on both sublattices must also be equal.
- A1/L1$_2$ ordering is often modelled with two sublattices (or 3 with interstitials) $(Ni,Al,Fe)_{0.75}(Al,Fe,Ni)_{0.25}(Va,C)_1$
- This model has many complicated relations between the parameters.

A1/L12 and A2/B2

FCC with A1 and L1$_2$ ordering $(A,B)_{0.75}(A,B)_{0.25}$

BCC with A2 and B2 ordering $(A,B)_{0.5}(A,B)_{0.5}$

Order/disorder

- A better description of ordering in FCC_A1 is obtained with four sublattices. In this case both $L1_2$ and $L1_0$ ordering can be described. The relations between the parameters are also simpler as all nearest neighbours are on another sublattice.
- Ordering in HCP_A3 using CEF is treated identically with ordering in FCC_A1.
- Order/disorder will be discussed again later

Selection of model parameters

- For the liquid and terminal phases the **excess parameters** can be optimized.
- For intermediate phases there are **Gibbs energy of formation parameters** to be optimized. Sometimes those are sufficients but for phases with large solubilities interaction parameters may be assessed also.

The setup file

- This is a macro file with commands to enter elements, phases, models, known parameters and model parameters to be assessed. See example tcex36

Other useful macro files

- Macro files for calculating phase diagram and various property diagram is very useful to have as looking at numbers does not really give enough information.

Numerical method for assessment

- The basic fitting is to vary the model parameters to minimize the difference between the experimental value and the same quantity calculated from the model.
- $Err = \Sigma_i \left((q_i^{exp} - q_i^{calc}) \, w_i/\sigma_i \right)^2$
- For each optimized variable in PARROT a "relative standard deviation" is listed. This indicates the uncertainity of the variable.

Using PARROT

- Run setup file
- Compile experiments
- Set alternate mode to optimize start values of parameters
- Selecting and weighting experiments and parameters to be optimized.
- Optimize will normal calculation and all experiments.

PARROT commands

|		
AMEND_PARAMETER	LIST_ALL_VARIABLES	REINITIATE
BACK	LIST_CONDITIONS	RESCALE_VARIABLES
COMPILE_EXPERIMENTS	LIST_PARAMETER	SAVE_PARROT_WORKSP
CONTINUE_OPTIMIZATI	LIST_PHASE_DATA	SET_ALTERNATE_MODE
CREATE_NEW_STORE_FI	LIST_RESULT	SET_FIX_VARIABLE
EDIT_EXPERIMENTS	LIST_STORE_FILE	SET_INTERACTIVE
ENTER_PARAMETER	LIST_SYMBOL_IN_GES	SET_OPTIMIZING_COND
EXIT	MACRO_FILE_OPEN	SET_OPTIMIZING_VARIAB
GOTO_MODULE	OPTIMIZE_VARIABLES	SET_OUTPUT_LEVELS
HELP	READ_PARROT_WORKSP	SET_SCALED_VARIABLE
INFORMATION	RECOVER_VARIABLES	SET_STORE_FILE

Alternate mode – start values

- One problem when starting the assessment is that many of the experimental data cannot be calculated. For example a tie-line between two phases may not exist unless the interaction parameters are between a certain range of values. The alternate mode makes it possible to calculate such experimental equilibria if some additional values are estimated.

Alternate mode

The two points represent compositions that should form a tie-line. But no equilibrium between the two phases can be calculated as there is no common tangent between the phases.

With the alternate mode the difference in chemical potential is minimized and that will force the points to be on a common tangent
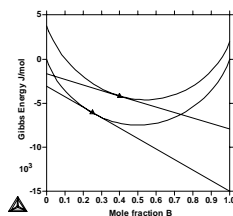
Alternate mode

The right figure have the Gibbs energy curves after using alternate mode.
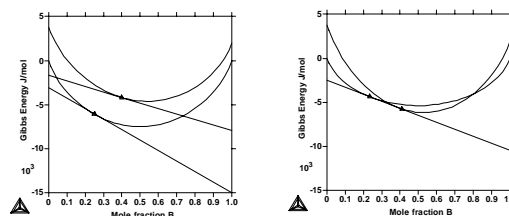
Optimizing by parts

- In a few cases an assessment may be done in one go but most often one will have to iterate several times using different weights and parameters to be optimized.

Kaufman/Ansara extrapolations

- For all solution phases calculate the extrapolations across the whole system with all pair of phases to check there are no unexpected features.
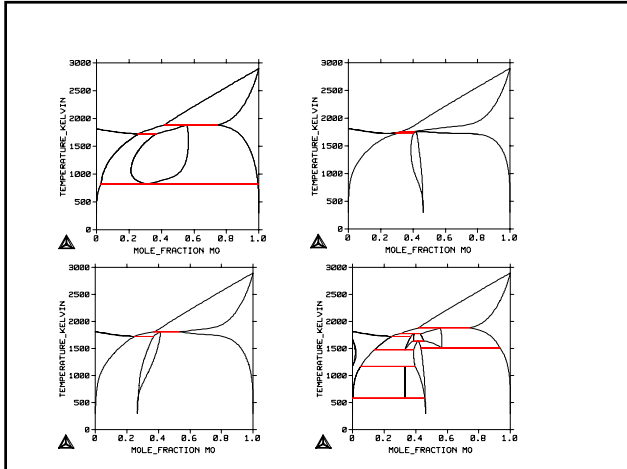
Assessment of ternary systems

- Many times when a ternary assessment is done one has to consider if the binary systems are really good enough. Ternary parameters have usually a small influence close to the binary sides.
- Solubilities of a third component in intermediate phases $(A)_a(B)_b$ becomes $(A)_a(B,C)_b$ – a metastable phase $(A)_a(C)_b$.

kursPM

- 2. Experimental and theoretical information, crystallography, enthapies, 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: Chaper 6.2 from book.
  Homework: TC example 36, testing different strategies.