Computer Calculation of Equilibria and Phase Diagrams

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4th lecture

Homework

- Prepare a floppy (or send E-mail) with the SETUP and POP file for the system you selected to the lecture next week! If you have trouble please ask for help
- Some classic homework assignments

Selection of parameters to optimize

- End-members are the first to optimize. Sometimes one has too many end-members and one may try to find relations between them to optimize fewer coefficients.
- Interaction parameters. If the phase has several sublattices one should optimize the interaction parameter on the sublattice with the largest number of sites.

- 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.

Selection of parameters to optimize

- In a ternary optimization one must not change or add parameters that affects any binary, unless that binary is reoptimized.
- When optimizing a metastable end-member to add a ternary solubility to a phase one must be careful that the phase does not become stable in the binary.

Selection of parameters to optimize

- Never use more parameters that supported by the amount of experimental data. Avoid Redlich-Kister coefficients higher than third degree, if such parameters seems necessary consider using another model.
- The relative standard deviation (RSD) for the coefficients at the end of an optimization should be less than 0.1. Use the RSD to round off the parameters in the end.

End-member parameters

- A sigma phase $(A)_{10}(B)_4(A,B)_{16}$ has 2 end-members. The first 10 sites are ”fcc” like with 12 nn, the other have 14-15 nn and are bcc like. The standard way to set these are
- G(sigma,A:B:A)=V1+V2*T+10*GFCCA+ 4*GBCCB+16*GBCCA
- Using no Tln(T) term means accepting the Kopp-Neuman rule that the heat capacity of the compound is equal to a linear combination of the heat capacity of the pure elements.
- The sigma phase is normally never stable all the way to the composition of the end-member

End-member parameters

- Some sigma phases with V and Cr exist outside the composition range given by the $(A)_{10}(B)_4(A,B)_{16}$ stoichiometry. One may then add a B element in first sublattice but the fraction of B on first sublattice should be low. One may manually adjust (rather than optimize) the parameter G(sigma,B:B:A) and G(sigma,B:B:B), to ensure this or include fictitious experimental data and optimize it. One may use the same coefficient for these parameters
- G(sigma,B:B:A)=V1+10*GFCCB+4*GBCCB+ . . 16*GBCCA
- G(sigma,B:B:B)=V1+10*GFCCB+20*GBCCB

End-member parameters

- To avoid reciprocal miscibility gaps one should ensure that the parameters in a reciprocal model, (A,B)(C,D), where at least one corner represent a meta-stable end-member, have the reciprocal reaction zero
- $G_{AC}+G_{BD}-G_{AD}-G_{BC} = 0$
- That gives a relation for the meta-stable parameter!

End-member parameters

For a ternary sigma phase one has parameters like G(sigma,A:B:C). There is usually not enough data to optimize these and one should first use the reciprocal reaction,

$G_{ABC}+G_{ACB}-G_{ABB}-G_{ACC}=0$.

For example use

G(sigma,A:B:C)=G(sigma,A:C:B)=
0.5*G(sigma,A:B:B)+0.5*G(sigma,A:C:C)

End-member parameters

- For the phases with order/disorder one can use the ”bond energies” as coefficients to be optimized. For the 4 sublattice ordered FCC there are 3 A-B bonds when 3 sublattices have A atoms and 1 B or vice versa, and 4 A-B bonds when two A and two B atoms. Thus
- G(fcc,A:A:A:B)=3*UAB+ 3*GFCCA+GFCCB
- G(fcc,A:A:B:B)=4*UAB+ 2*GFCCA+2*GFCCB
- G(fcc,A:B:B:B)=3*UAB+ GFCCA+3*GFCCB

Interaction parameters

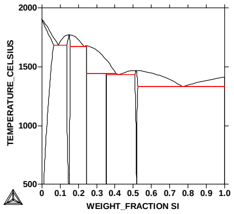
- The binary interaction parameter, L_{AB} can be composition dependent through a Redich-Kister series. Beware to use too many coefficients, especially if the phase is stable only in a small composition range.
- Ternary and higher order parameters should be considered as the composition dependence of the binary parameters. First try to modify the binary parameters to get the correct extrapolation.

Parameters in metastable phases

- Some phases may not be stable in a binary but one may anyway have to estimate parameters for them as both elements may dissolve in such a phase inside a ternary system.
- The standard method is to set the interaction parameters equal to some phase stable in the binary

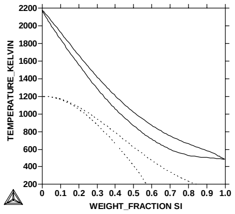
Parameters in Cr-Si

The BCC is stable in only a small composition range in Cr-Si and there is no FCC phase at all.



Parameters in Cr-Si

The metastable phase diagram for BCC/LIQ and FCC/LIQ for Cr-Si.



Parameters in Cr-Si

- L(LIQ,CR,SI;0) = -20157.52+16.63891*T
- L(LIQ,CR,SI;1) = -49502.35+13.76967*T

- L(BCC,CR,SI;0) = -102850.19+9.85457*T
- L(BCC,CR,SI;1) = -49502.35+13.76967*T

- L(FCC,CR,SI;0) = -122850+9.85457*T
- L(FCC,CR,SI;1) = -49502+13.76967*T

Modelling the liquid phase

- The liquid phase is certainly the most challenging phase to model as its properties may vary a lot within a continuous solution.
- The liquid phase often forms a continuous solution between the elements but sometimes there are miscibility gaps

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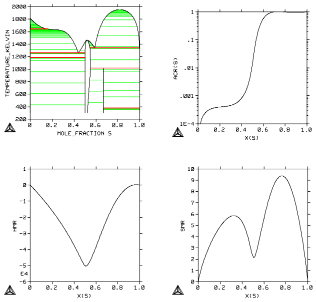
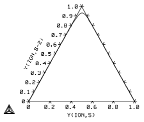
Thermochemical properties for Fe-S



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



Modelling the liquid phase

- In a liquid the atoms positions are not fixed relative to each other, there is no long range order (lro).
- Small groups of like or unlike atoms may cluster together in the liquid, this is known as short range order (sro).

Modelling the liquid phase

- Special behaviour of data, like strong ”V” shaped enthalpy of mixing (sharp raise of activity) indicates sro.
- The composition of the sro is always close to a solid compound (FeS) or a gas species

Modelling the liquid phase

- 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 the regular solution is often not good and an *associated, quasichemical* or *ionic liquid* model may be used instead.

Associated model

- The model assumes that one or more ”associates” are formed in the liquid. The associate have all the properties of a real species but cannot be verified by experimental methods (if the species can be verified experimentally then it is no longer an asociated model but a reality)

Associated model

- $G_m = x_A{}^0G_A + x_{AB}{}^0G_{AB} + x_B{}^0G_B + RT(x_A\ln(x_A) + x_{AB}\ln(x_{AB}) + x_B\ln(x_B)) + {}^EG_m$
- ${}^EG_m = x_A x_{AB} L_{A,AB} + \dots$
- When the liquid is pure AB the configurational entropy is almost zero

Associated model

- Advantages: Simple and easy to use
- Disadvantages: Extrapolations to higher order systems require additional interactions between the associates. It does not become ideal (as the quasichemical model) if the energies ${}^0G_{AB} = 0$.

Quasichemical model

- Based on the mixing of ”bonds” rather than atoms. If one has bonds AA, AB and BB the entropy of mixing can be written
- $S_m=-Rz(x_{AA}\ln(x_{AA})+2x_{AB}\ln(x_{AB})+x_{BB}\ln(x_{BB}))$
- Z is half the number of bonds between A and B
- The factor 2 comes from the fact that a bond AB has a direction, AB or BA.

Quasichemical model

- The previous entropy expression overestimates the entropy and must be corrected to give the ideal entropy of mixing when there is no sro. The corrected entropy expression is
- $S_m=-Rz(x_{AA}\ln(x_{AA})+2x_{AB}\ln(x_{AB})+x_{BB}\ln(x_{BB})) + R(2z-1)(x_A\ln(x_A)+ x_A\ln(x_A))$
- With no sro $x_{AA}=x_Ax_A$, $x_{AB}=x_Ax_B$, $x_{BB}=x_Bx_B$.

Quasichemical model

- The reference energy expression is

$x_{AA}\ {}^0G_{AA} + x_{AB}\ {}^0G_{AB} + x_{BB}\ {}^0G_{BB}$

Quasichemical model

- Advantages: Physically correct behaviour when the liquid becomes ideal. Rather simple to handle.
- Disadvantages: The value of z is not known in the liquid and it is complicated to let it vary with composition. Many different excess models are used.

Quasichemical model

- If z >2 and the sro is strong the quasichemical model gives negative entropies which is unphysical. For crystalline solids this never happen as the material will develop long range order but for liquid there is no long range order.

Ionic liquid model

The ionic liquid model one starts from the rather unphysical assumption that one has long range order in the liquid. This may seem very drastic but for an ionic liquid one may consider distributing the anions and cations separately at their positions in space. It would be very unlikely (require a lot of energy) to place a cation in a place where there has been an anion.

Ionic liquid model

- The first ionic liquid model was proposed by Temkin 1945 for molten salts. It assumed one sublattice for anions and one for cations $(C^{+c})_P(A^{-a})_Q$. P and Q must vary with composition to ensure electroneutrality.
- Instead of using P and Q one can define ”equivalent fractions” z_A as follows
- $z_A = v_A x_A/(v_A x_A + v_B x_B + \ldots)$
  where v_A is the charge of ion A and x_A the mole fraction of A

Ionic liquid model

- Many liquids change in character with composition. For example Cu-Fe-S has metallic behaviour along Cu-Fe but ionic behaviour along Cu-S and Fe-S. A model to describe this ternary must handle both these behaviours.

Ionic liquid model

- In 1984 Hillert extended the Temkin model by adding hypothetical vacancies to the anion sublattice. It was also allowed to have neutral species there. But the cation sublattice could only contain cations. $(C^{+c})_P(A^{-a},Va,K^0)_Q$
- P and Q vary with composition and are calculated as the average charge on the opposite sublattice.
- The vacancies are assumed to have an ”induced” charge equal to Q.

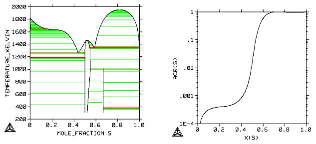
Ionic liquid model

- The new model described metallic subsystems as a regular solution by having only Va in the anion sublattice $(Fe^{+2},Cu^{+1})_P(Va)_Q$
- Systems like Fe-C where C is assumed to have no tendency to take or give electrones can be modelled as $(Fe^{+2})_P(Va,C)_Q$ which turns out to be identical to a regular solution model Fe-C.

Ionic liquid model

- Most surprisingly the ionic model for Fe-S, $(Fe^{+2})_P(S^{-2},Va,S^0)_Q$ turned out to be identical to the associated model (Fe, FeS,S)

Thermochemical properties for Fe-S



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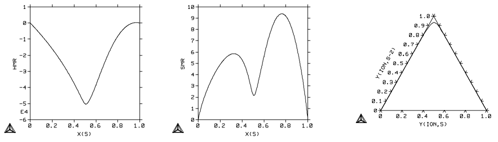


Ionic liquid model

- For oxides and other systems the ionic liquid model has been used extensivly, for example Ca-Fe-Si-O modelled as $(Ca^{+2},Fe^{+2},Si^{+4})_P(O^{-2},SiO_4^{-4},Va,SiO_2,FeO_{1.5})_Q$

Ionic liquid model

- Advantages: Can handle all types of liquid phases (except aqueous solutions)
- Disadvantages: The model has a strong tendency to form reciprocal miscibility gaps that are difficult to control.

Solid metal-nonmetal phases

- Examples of such phases are carbides, nitrides, oxides, sulphides etc.
- Unless the constituents are charged one can model these with a normal CEF. In the simplest case the metals occupy one sublattice and the non-metal another like in M_7C_3. In other cases more sublattices are needed.

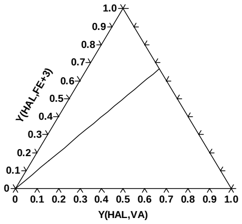
Solid metal-nonmetal phases

- Some carbides, nitrides etc have the same structure as some metallic phases, like the cubic carbonitride (Nb,Ti,V,…)(C,N,Va) which has the same structure as the interstitial solution of C or N in austenite.

Solid metal-nonmetal phases

- If the phase has charged constituents, ions, one have to consider defects and the charge balance. For wustite, approximately FeO, some Fe is always trivalent and the model to use is $(Fe^{+2},Fe^{+3},Va)_1(O^{-2})_1$.
- This model has three end-members, two of which are charged. Only neutral combinations of charged end-members have any physical significance. Note the vacanices are neutral!
- One may have charged vacancies in a solid phase representing electrones or holes.

Halite (wustite) neutral range



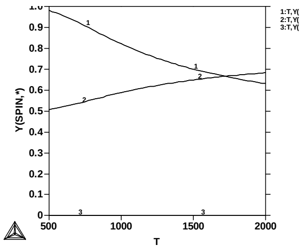
Halite parameters

- Note the end-member G(halite,Va:O^{-2}). This parameter should be set to zero as it will appear in all halite phases, not just wustite.
- For ionic phases one arbitrary parameter can be set to zero as that represent the energy of creating an ion.

Solid metal-nonmetal phases

- More complicated phases like the magnetite, Fe_3O_4which is a spinel, can have several sublattices with charged constituents $(Fe^{+2},Fe^{+3})_1(Fe^{+2},Fe^{+3},Va)_2(O^{-2})_4$

Site fractions in spinel (Fe_3O_4)



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- 4: Selection of parameters to optimize. Modelling liquids. Modelling metal-nonmetal phases