A global approach of the liquid Gibbs energy
-
Calphad modeling

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Outline

- Calphad thermodynamics: basic principles
- Thermodynamic models for the liquid phase
  - Structural models
    - (Sub-) regular solutions – the Bragg-Williams model
    - Introducing short range order
      - Associate model (Predel / Sommer)
      - Modified quasi-chemical model (Chartrand / Pelton)
      - Ionic liquid model (Hillert / Sundman)
  - What about the glass transition ?
    - Two-state model (Agren)
- Conclusions

Calphad thermodynamics : basic principles

- Thermodynamic equilibrium = Minimisation of the total Gibbs energy of the system (@ constant T,P)

$$G(T,P,x_i)=\sum_j x_j G_j(T,P,x_i)$$

G_i : Gibbs energy of phase i

T : temperature

P : total pressure

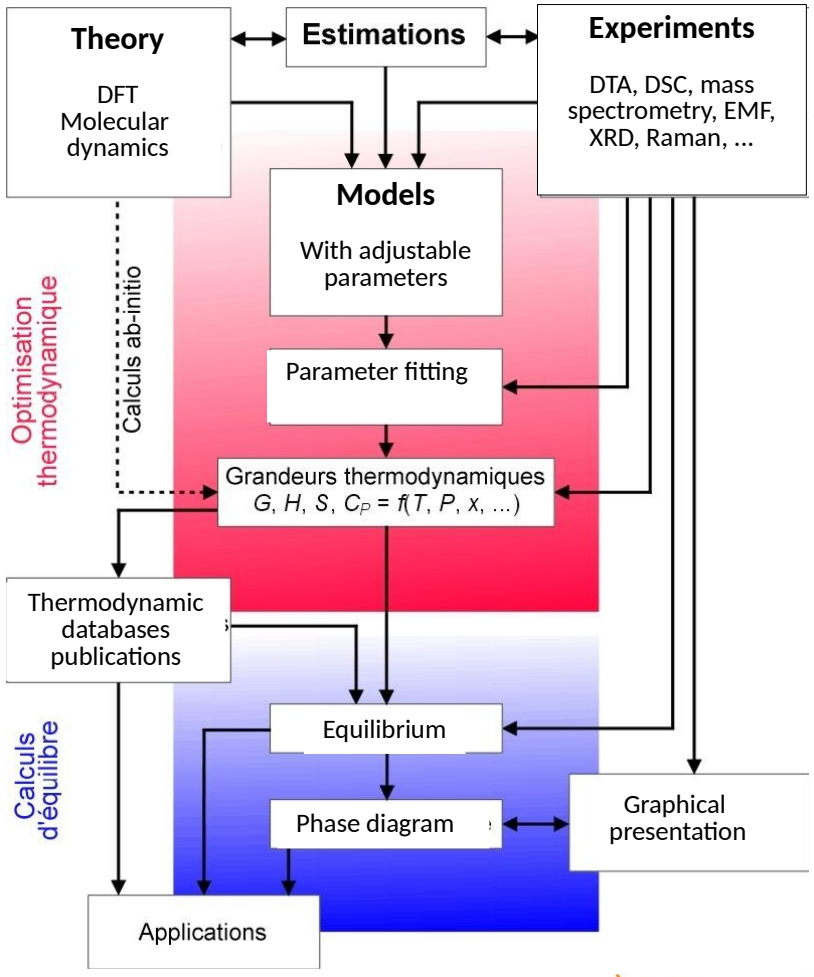
x_i : composition of chemical species i

- Minimum of G with respecting mass balance + other constraints (electroneutrality …)
- Alternative view: Phase distribution (type and amount) for which G becomes a minimum

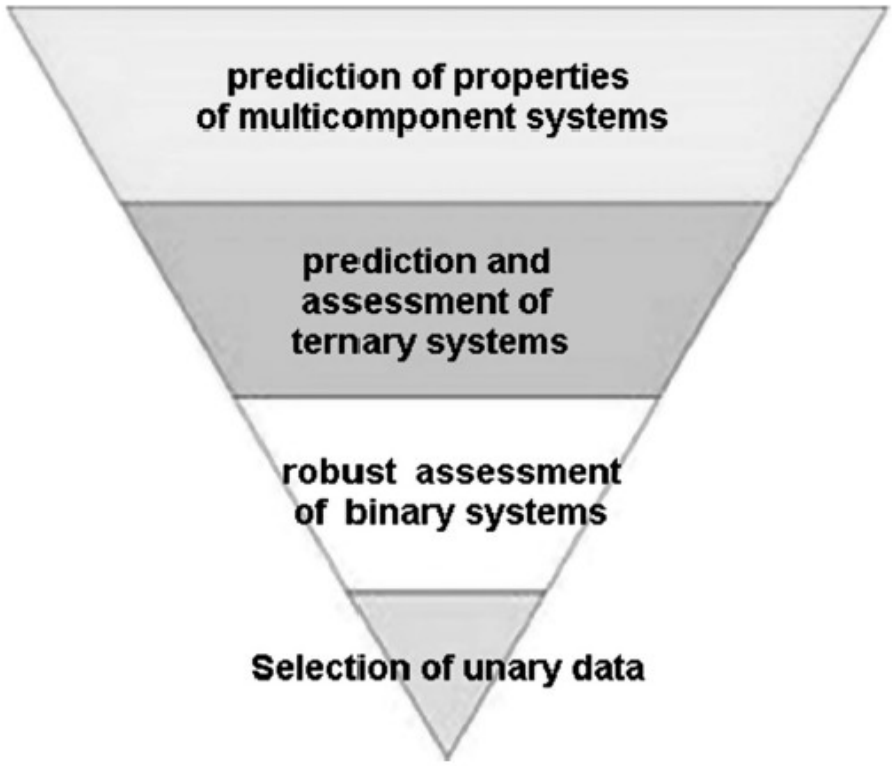
Calphad thermodynamics : basic principles

- Gibbs energy minimization software
  - Commercial
    - Thermocalc AB
    - Factsage (GTT Technologies)
    - MTData (Hampton Thermodynamics)
    - Pandat (Computherm LLC)
    - OLI [aqueous]
  - Free / Open source
    - OpenCalphad (http://www.opencalphad.com)
    - PyCalphad (https://pypi.org/project/pycalphad/)
    - GEMS (http://gems.web.psi.ch/overview.html) for aqueous systems
    - PhreeqC (https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) for aqeuous systems

Calphad thermodynamics : basic principles



Calphad thermodynamics : database development



Unary data

- Elements (Al, Hg, O_2(g) …)
- Simple Oxides (CaO, Al_2O_3, SiO_2,…)
- Halides (NaCl, $CaCl_2$)
- Sulfates ; Phosphate ; Hydroxides ; ….

Calphad thermodynamics : database development

$$G = \Delta H - T * S$$

$$\Delta H(T) = \Delta H(0\,K) + \int_{0\,K}^{T} C_p\, dT$$

$$S(T) = S(0\,K) + \int_{0\,K}^{T} \frac{C_p}{T}\, dT$$

$$C_p = a + b*T + c*T^2 + d*\frac{1}{T^2}$$

Stoichiometric compounds

- Elements: Mg, Si, O_2(g) …
- Compounds: $CaSi_2$, MgO, NaCl…
- End members of solutions (!)

Complex gas phase

- Ideal gas pV=nRT

$$G^{gas} = \sum_{i}^{n} x_i \left(G_i^0 + RT \ln\left(\frac{P_i}{P^0}\right)\right)$$

P_i partial pressure of gas species i

P^0 reference total pressure

Calphad thermodynamics: database development

Solution phases

- Solid solutions
  - Disordered : e.g. FCC_A1, BCC_A2 …
  - Ordered phases : e.g. $L1_2$
- Liquid solutions
  - Molecular
    - weak interaction, v.d. Waals: H_2O
  - Metallic
    - atomic distribution in an electron cloud: Au-Ag
  - Covalent
    - strong structural aspect: SiO_2
  - Ionic
    - Coulombian forces, electronic charges & ion radius: molten salts
  - Other
    - Polymers, liquid crystals

Thermodynamic modeling of the liquid phase

Gibbs energy of any solution is additive: $G^{sol} = G^{ref} + G^{id} + G^{exc}$

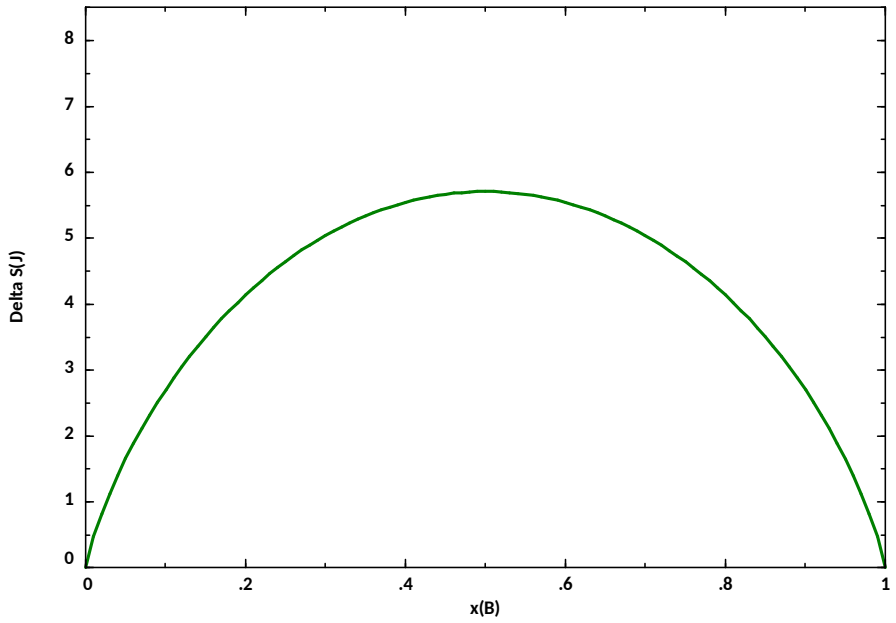
$G^{ref} = \sum_i x_i G_i^0(T, P, x_i)$ Reference Gibbs energy “mechanical mixture”

$G^{id} = T * S^{id} = RT \sum_i x_i \ln(x_i)$ Ideal mixing

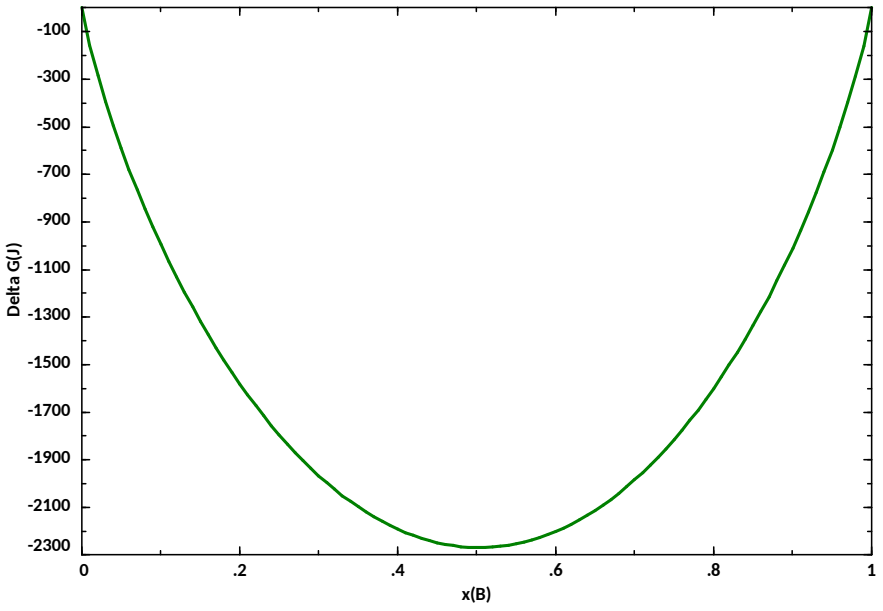
G^{exc} Excess Gibbs energy due to mixing

Thermodynamic modeling of the liquid phase

$$G^{id} = T * S^{id} = RT \sum_i x_i \ln(x_i)$$



Ideal entropy



resulting Gibbs energy @420K

Model : (Sub-)regular solution

- Enthalpy difference between A+B and solution (AB) ≠ 0

  → mixing generates or consumes heat

- The molar enthalpy of the solution can be evaluation from the pair interaction

  $[A\text{-}A]_{pair}+[B\text{-}B]_{pair} = 2\,[A\text{-}B]_{pair}$

  with the total energy for two pairs: $\Delta E_{AB} = 2\,E_{AB}-E_{AA}-E_{BB}$

  one gets for the mixing energy $G^{exc}= x_A x_B \omega_{AB}$ → regular solution

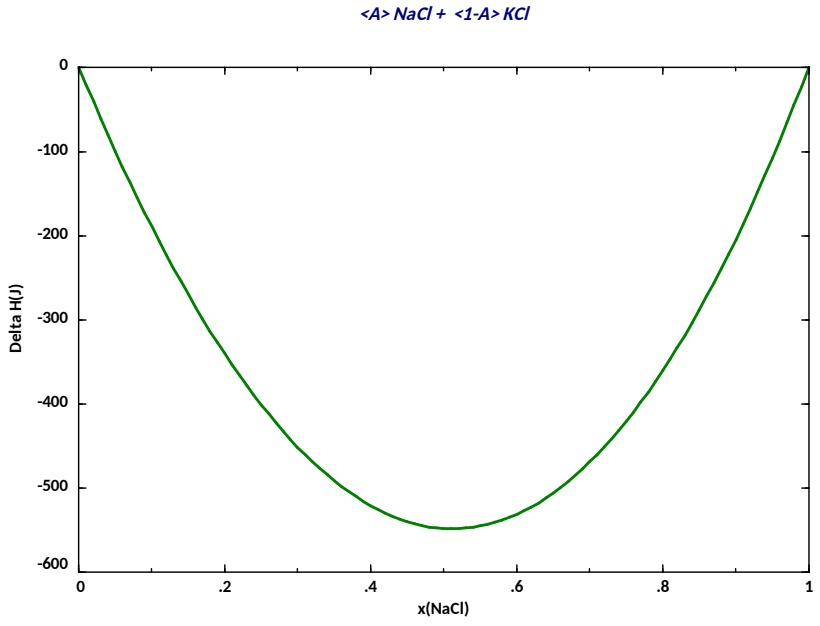
  ω_{AB} can
  - be a constant = configurational entropy is ideal
  - depend on temperature = configurational entropy is taken into account
  - depend on other parameters (pressure, ionic radius…)

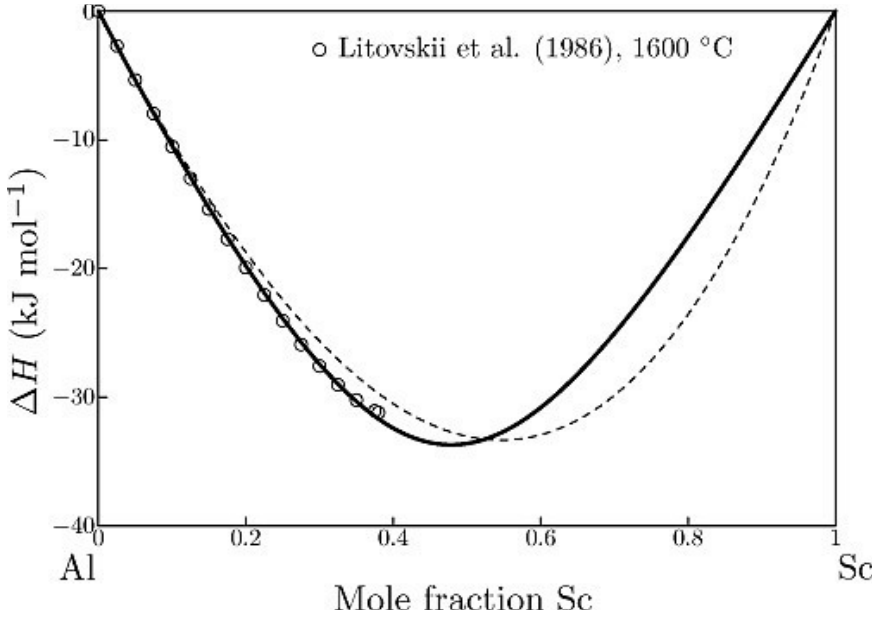
Model : (Sub-) regular solution

- Chemically similar species can be described by a regular solution model

- model can be applied for solid and liquid phases

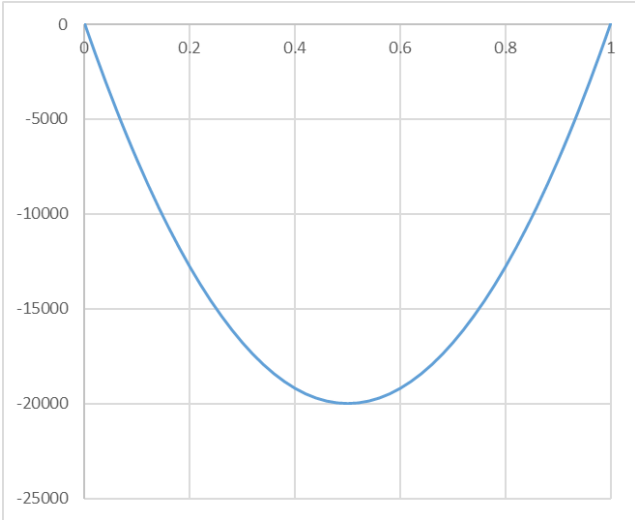
- interaction is weak and very low tendency for short range order



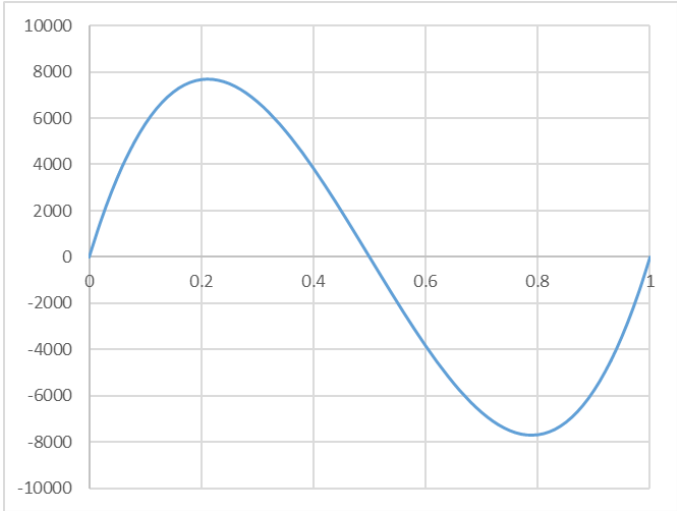


Model : (Sub-) regular solution

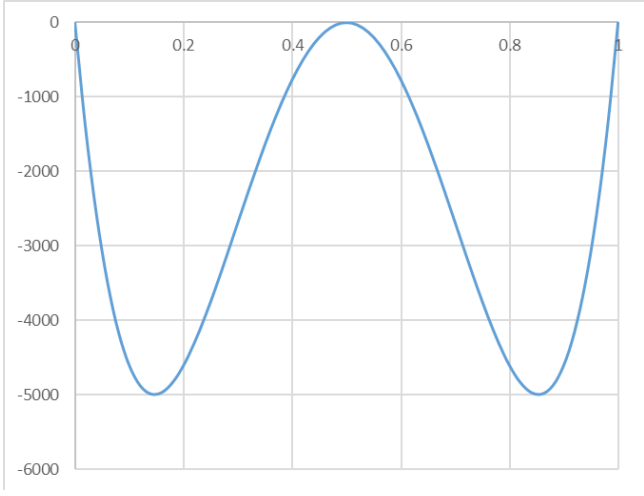
Redlich Kister polynomials $$G^{exc} = x_A x_B \sum_0^n (x_A - x_B)^n L_{AB}^n$$



n=0



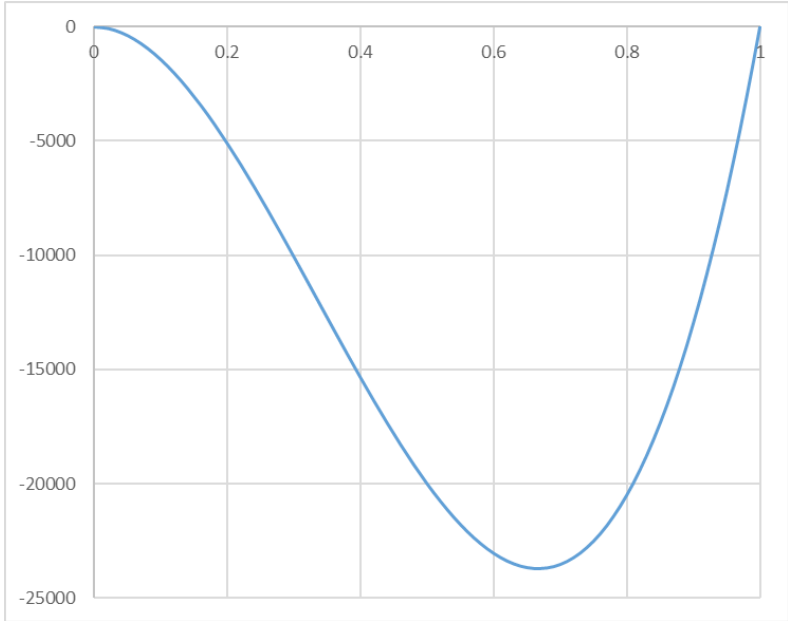
n=1



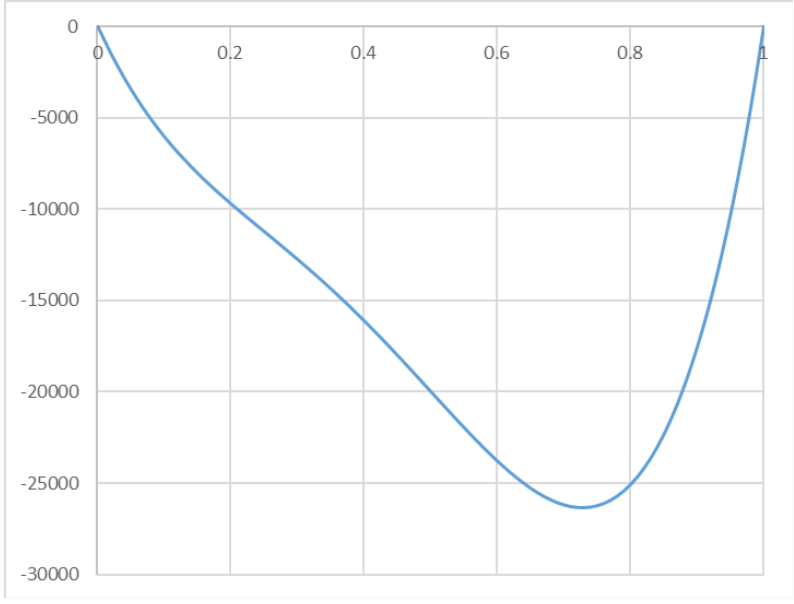
n=2

Model : (Sub-) regular solution

Redlich Kister polynomials $$G^{exc} = x_A x_B \sum_0^n (x_A - x_B)^n L_{AB}^n$$

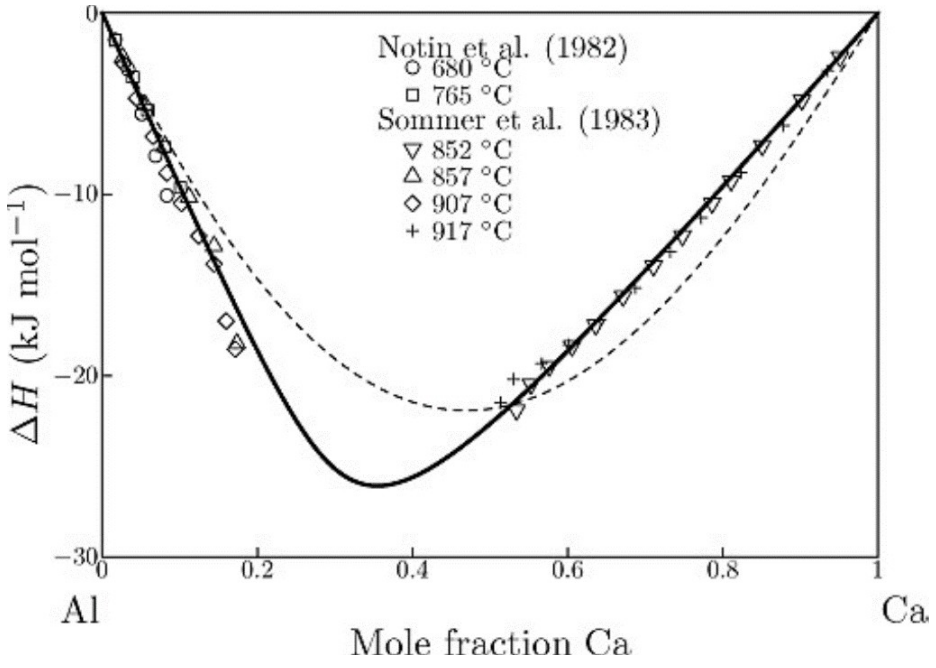


n=0,1



n=0,1,2

Calphad modeling: (Sub-) regular solution



Short range ordering

- (Sub-) regular model is not suited for systems with strong tendency for short range order
  - Al-Y, Mg-Si …
  - Metal-oxide (Ca-CaO), metal-fluoride …
  - Oxide-oxide system (Na_2O-SiO_2, Na_2O-Al_2O_3,…)
  - Reciprocal systems: NaF-CaF_2-NaCl-$CaCl_3$

- Models to describe short range order
  - Associate model (Predel / Sommer)
  - Quasi-chemical model (Fowler / Guggenheim / Pelton /Blander / Chartrand)
  - Ionic liquid model (Hillert/Sundman)

Short range ordering : associate model

- Model developped by Predel & Sommer (Univ. Stuttgart, Germany)
- Basic assumption
  - Two species are “bound” together (= form an associate) so that they can be considered as an individual particle/complex
- The Gibbs energy for the solution phase becomes (e.g. associate AB)

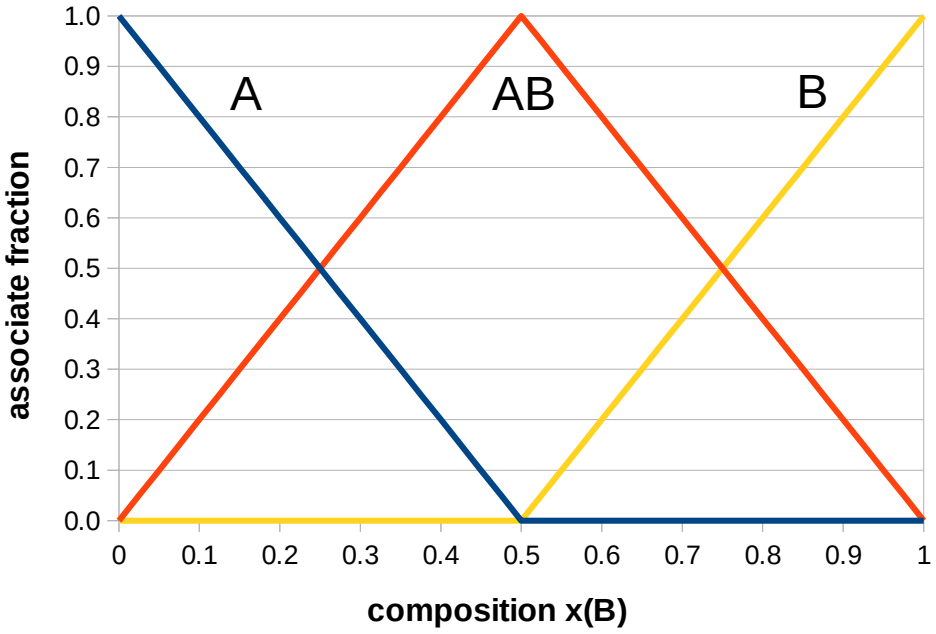
$$G^{ref} = \sum_i x_i G_i^0(T, P, x_i)$$

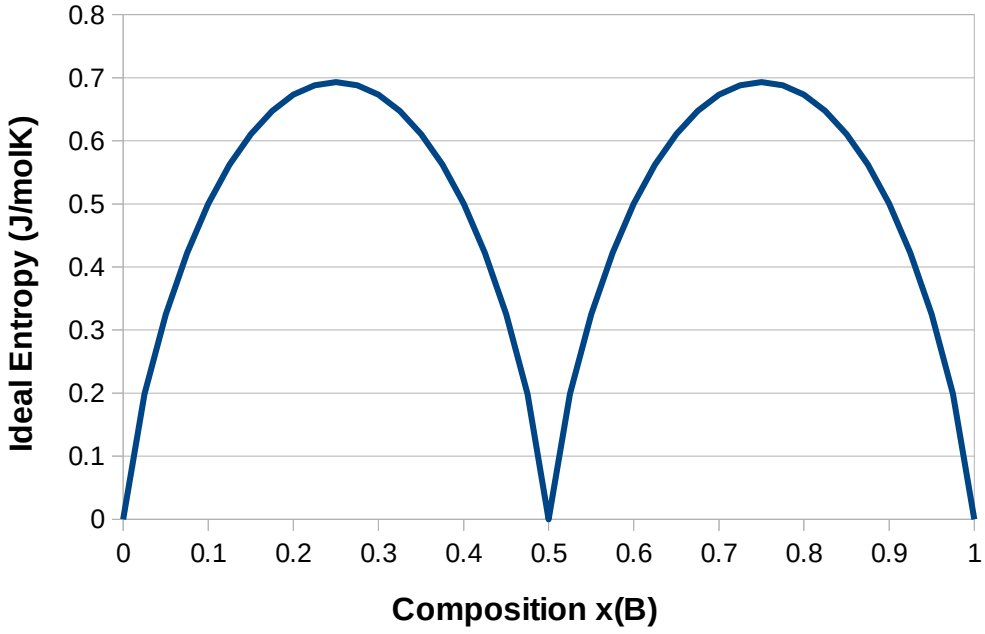
i = A, B, AB

$$G^{id} = T * S^{id} = RT \sum_i x_i \ln(x_i)$$

$$G^{exc} = x_A x_B \sum_0^n (x_A - x_B)^n L_{A-B}^n + x_A x_{AB} \sum_0^n (x_A - x_{AB})^n L_{A-AB}^n + x_{AB} x_B \sum_0^n (x_{AB} - x_B)^n L_{AB-B}^n$$

Short range ordering : associate model

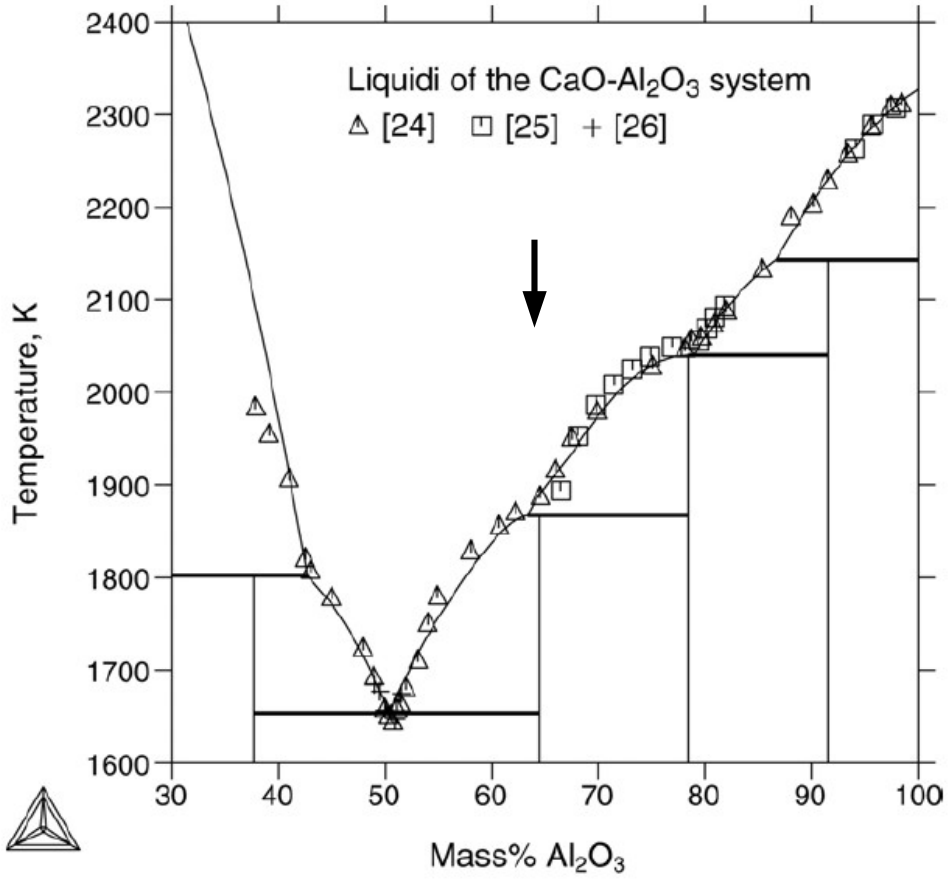


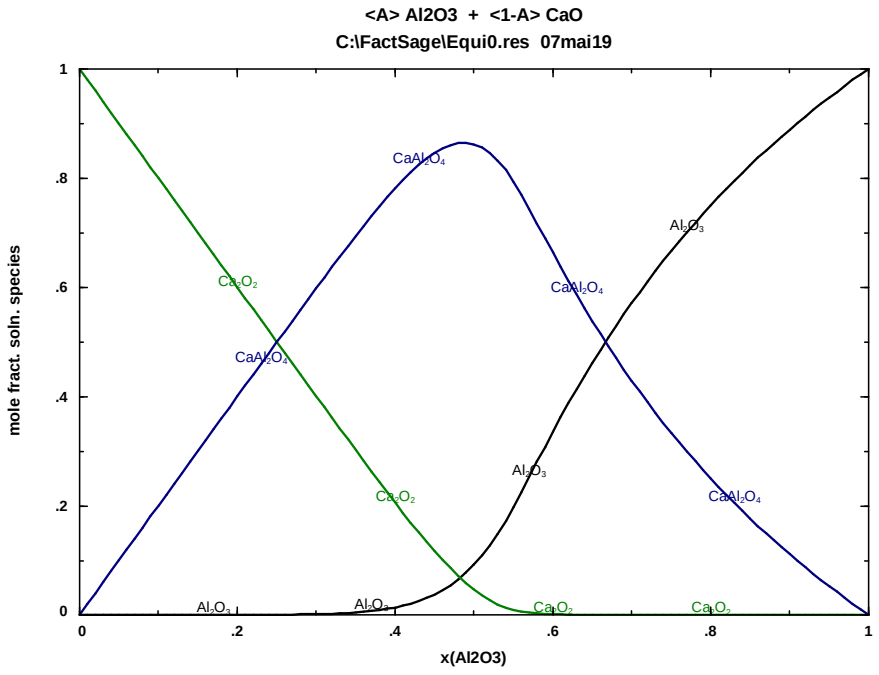


How to choose the associates ?

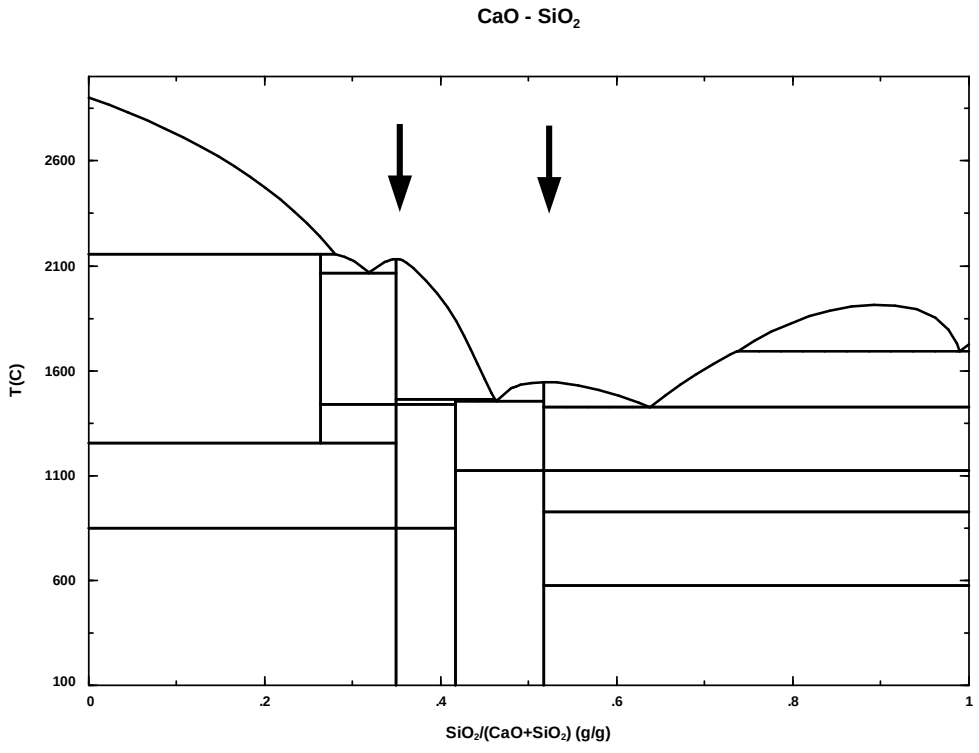
- The choice of the associates is arbitrary and have not always a physical meaning !
- Ideally, start from experimental information
  - Raman
  - NMR  Q^n-species
  - XANES
  - …
- Examples
  - GTOx: Ca_2O_2, Si_2O_4, Al_2O_3, Na_2O, 2/3 Ca_2SiO_4, $CaSiO_3$, 2/3 $CaAl_2O_3$, 2/5 Na_4SiO_4 …
  - MTox: CaO, $AlO_{3/2}$, SiO_2, MgO, $CaSiO_3$, $SiAl_{4/3}O_4$…

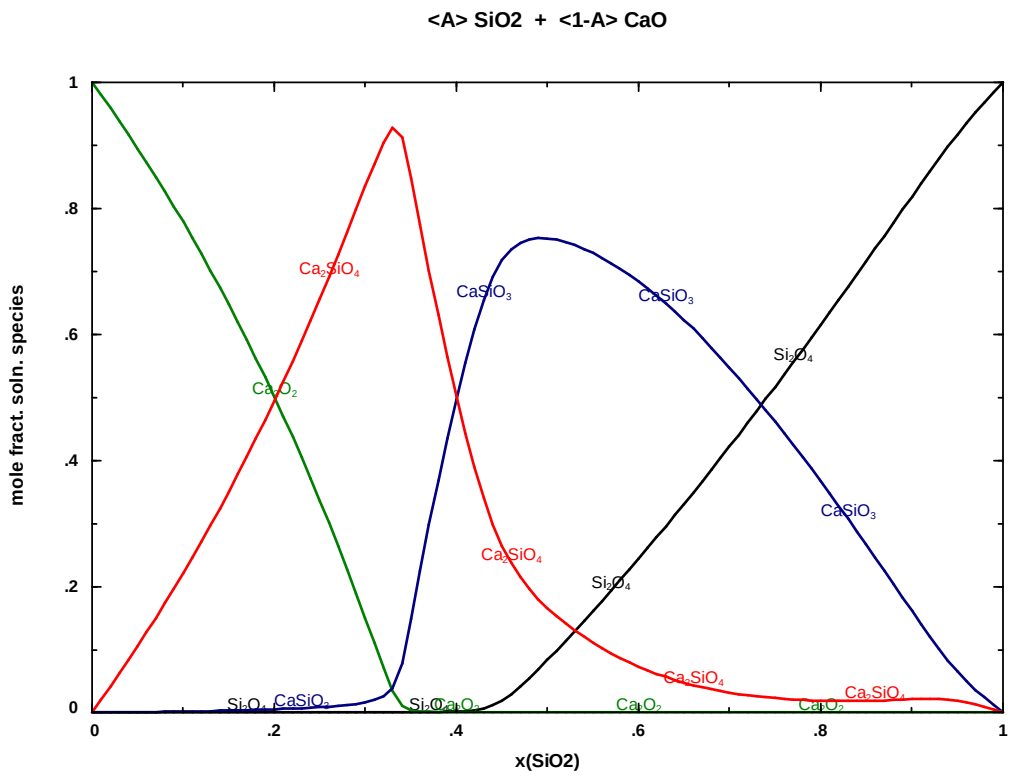
Associate model : $CaO\text{-}Al_2O_3$





Associate model : $CaO\text{-}SiO_2$





Potential associates: CaO, Al2O3

Short range ordering : Quasi-chemical model

Impact of the pair interaction on the configuration

– Introduced by Fowler &Guggenheim (1939)

- The configurational entropy and the mixing enthalpy depend on the pair interaction energy

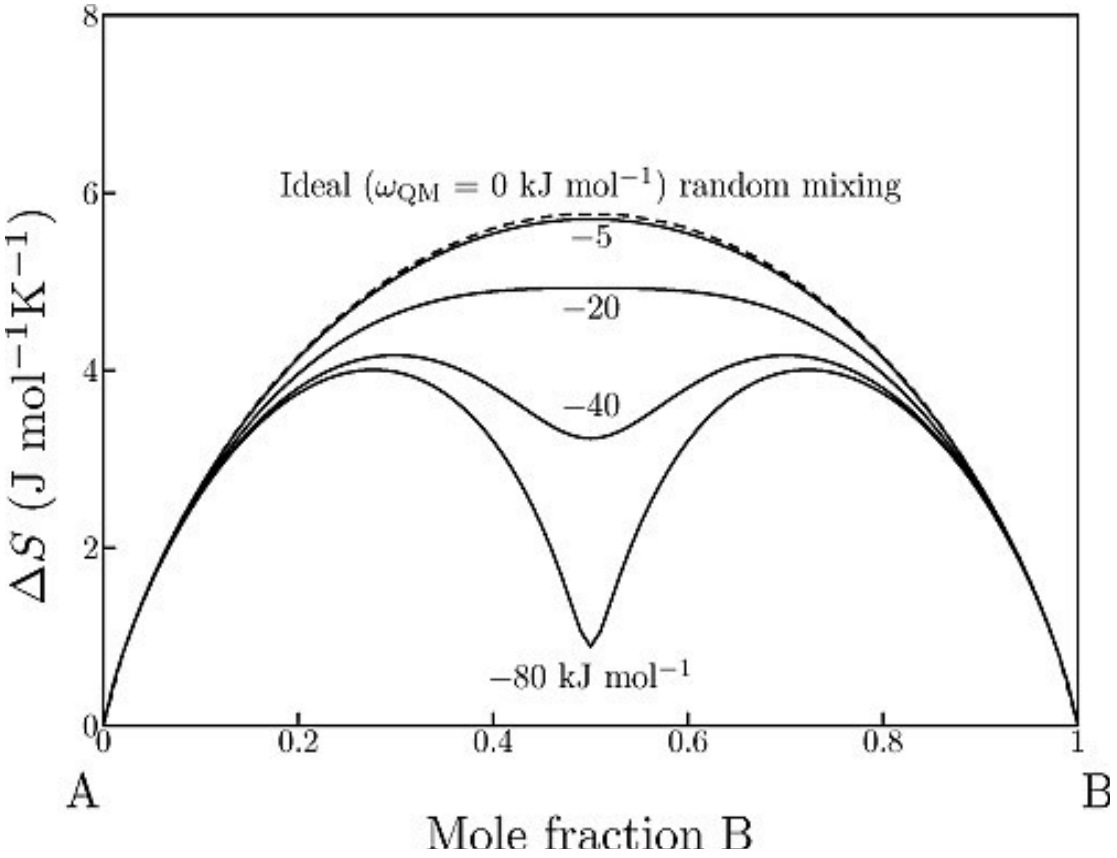
  $[A\text{-}A]_{pair}+[B\text{-}B]_{pair}=2\,[A\text{-}B]_{pair}$ $\Delta g_{AB} = \omega_{AB}-\eta_{AB}T$

- Allows to evaluate the short range order tendency of a solution
- The configurational entropy expression is derived from the Ising model

$$S^{config} = -R\left(x_A \ln\left(x_A\right)+x_B \ln\left(x_B\right)\right)-R\left(x_{AA} \ln\left(\frac{x_{AA}}{x_A^2}\right)+x_{BB} \ln\left(\frac{x_{BB}}{x_B^2}\right)+x_{AB} \ln\left(\frac{x_{AB}}{x_A x_B}\right)\right)$$

- If ω_{AB}=O, the configuration entropy becomes identical to the ideal entropy

Short range ordering : Quasi-chemical model

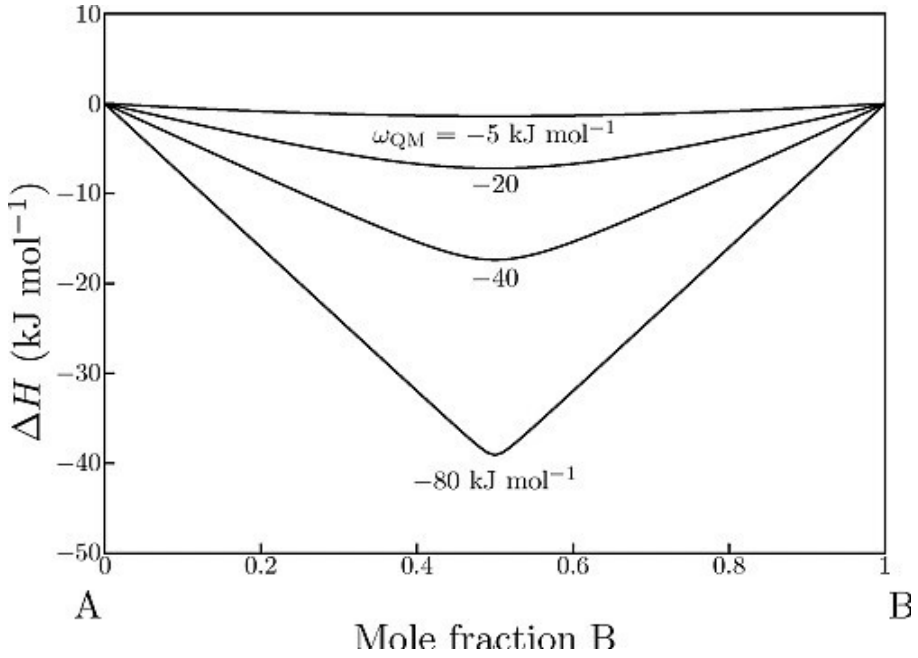


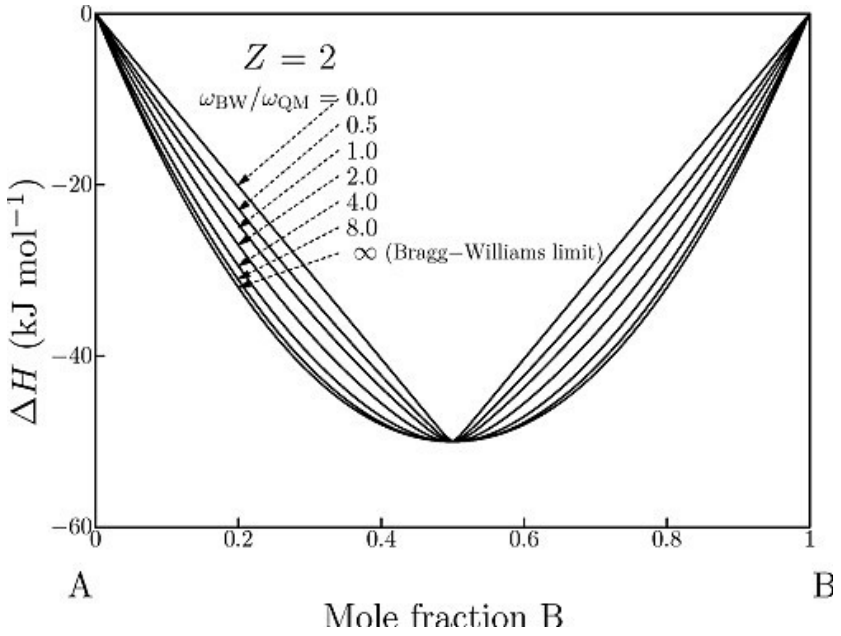
Configurational entropy

ω_{AB}= 0 → ideal entropy

ω_{AB} < 0 → ordered solution
(AB pair formation)

Short range ordering : Quasi-chemical model





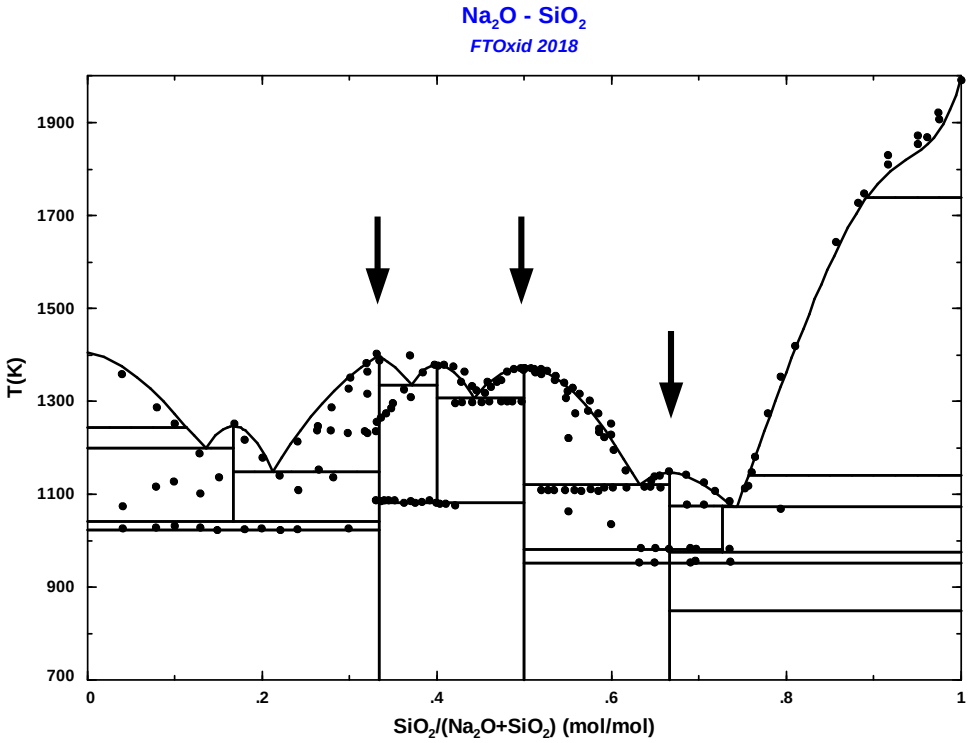
Short range ordering : Quasi-chemical model

- Modification of Pelton & Blander (1984,1986)
  - The minimum of the mixing enthalpy (=maximum short ranger order) can be shifted
    → equivalent fractions replace mole fractions of the species
  - Consequence: the Ising configurational entropy is no longer exact and becomes an approximation
  - Pair formation energy becomes composition dependent
    → the enthalpy curve can be modelled more round
- Modification from Pelton&Chartrand
  - Introduction of two sublattices (cations/anions) to describe first neighbor / second neighbor interaction
    → quadruplets

    Example: Metal-Si-O-Cl

    unary quadruplet: Si-O-Si-O …
    binary quadruplet: Si-O-M-O, Si-O-Si-Cl …
    reciprocal quadrulplet: Si-O-M-Cl

Quasi-chemical model : Na_2O-SiO_2

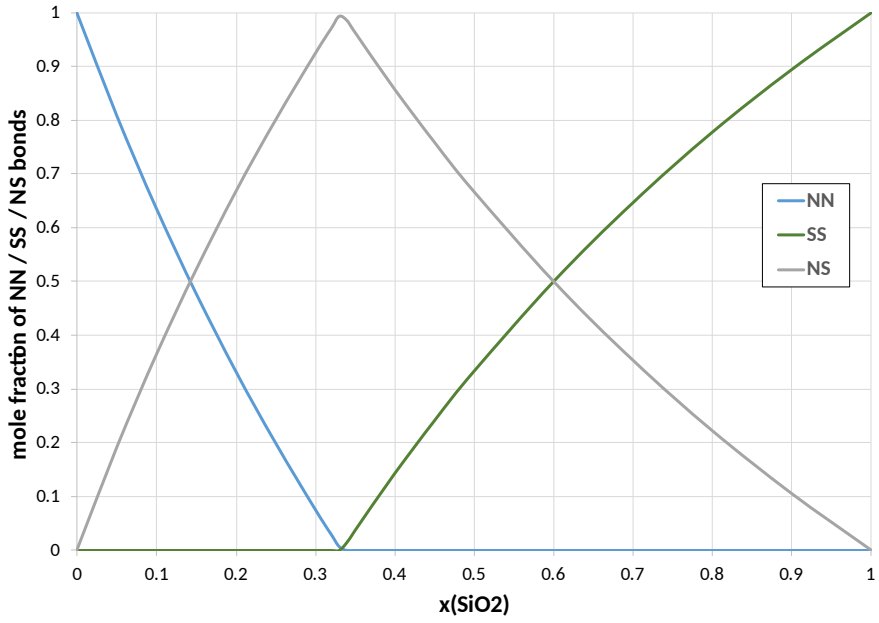


Experimental
Q^4, Q^3, Q^2

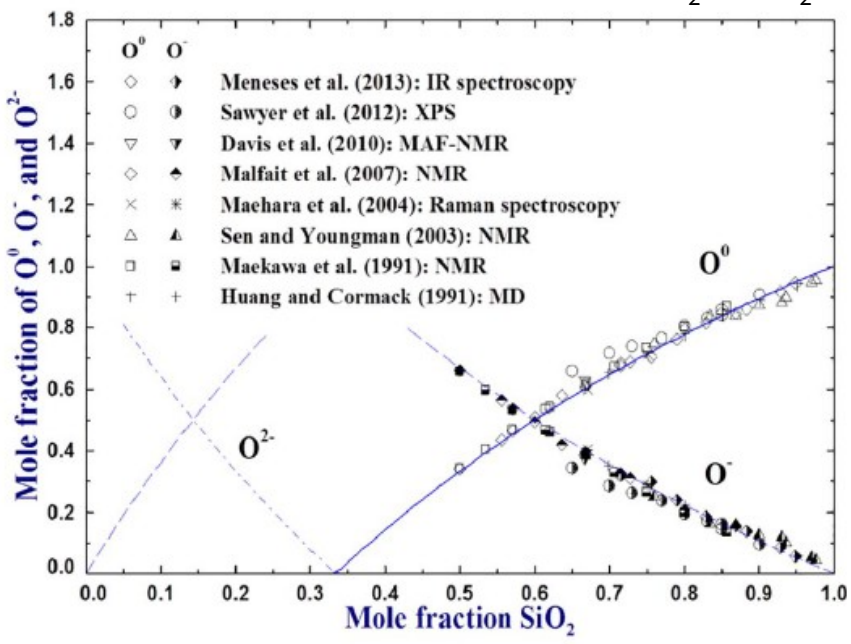
Associate model
SiO_2, $Na_2Si_2O_6$, Na_2SiO_3, Na_4SiO_4, Na_2O

Quasi-chemical model
Na-O-Na, Si-O-Si, Na-O-Si

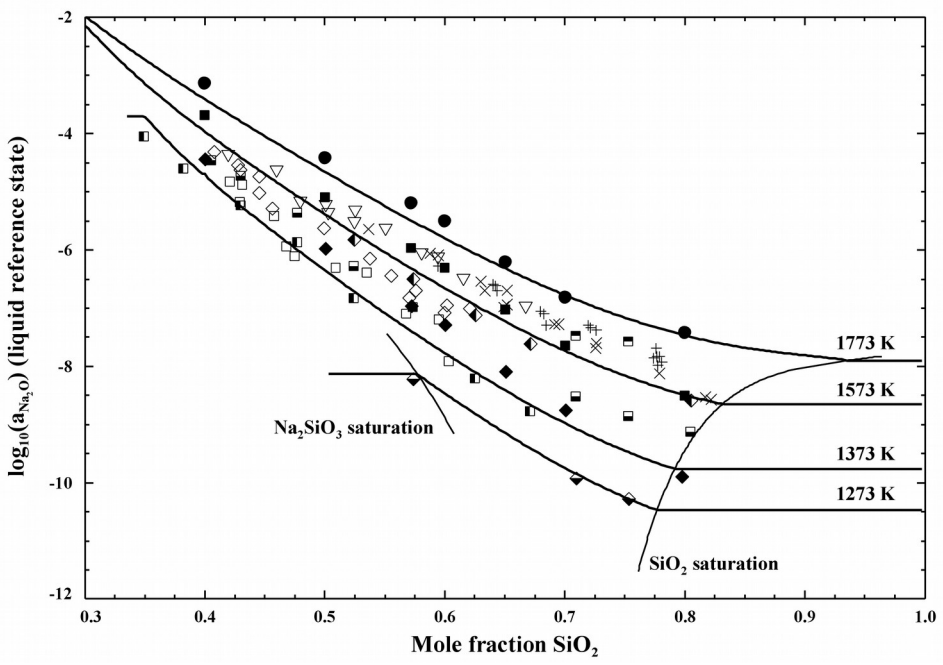
Quasi-chemical model : Na_2O-SiO_2

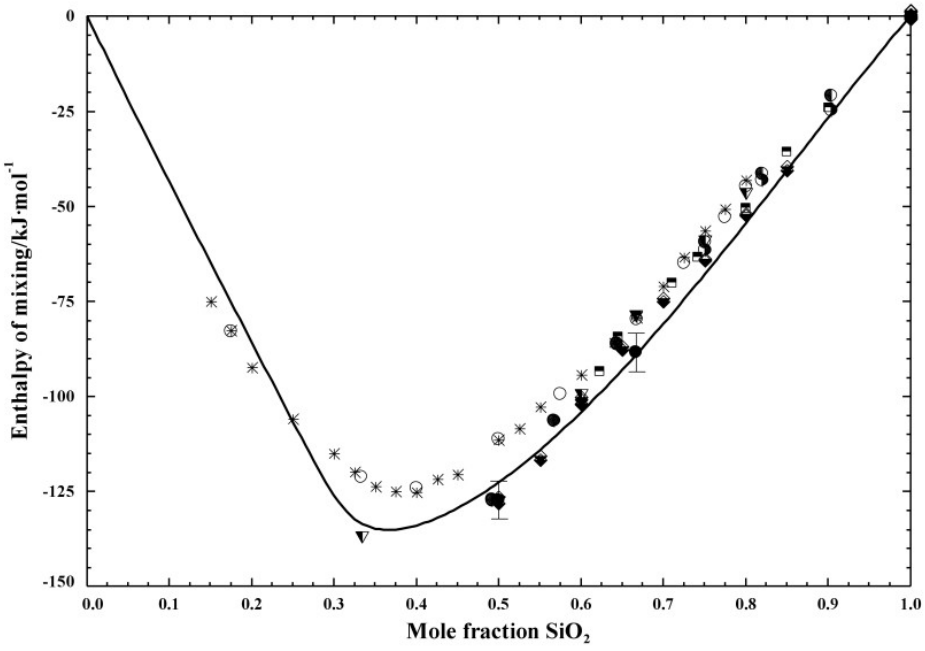


K_2O-SiO_2



Quasi-chemical model : Na_2O-SiO_2





Quasi-chemical model : Q^n species

- **From pair fractions → Q species**

total O in liquid: $n_t = ½\ x(NaO_{0.5})+2x(SiO_2)$

bridging O n_O for Si-Si pairs: $n_O = x(Si\text{-}Si)*n_t$

amount of $x(SiO_2)$ in 1 mol liquid : $2\ n_O / x(SiO_2)$

Probability that O is a bridging O

$$p = (2\ n_O / x(SiO_2))/4 = n_O / 2x(SiO_2)$$

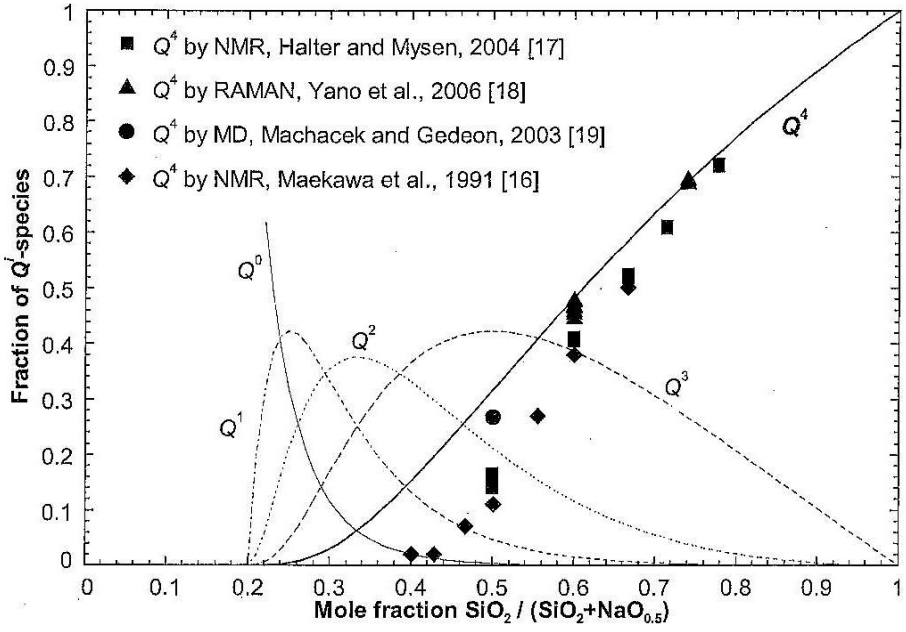
Equivalent fraction of SiO_2

$$Y(SiO_2) = 4\ x(SiO_2) / (4x(SiO_2)+x(NaO_{0.5}))$$

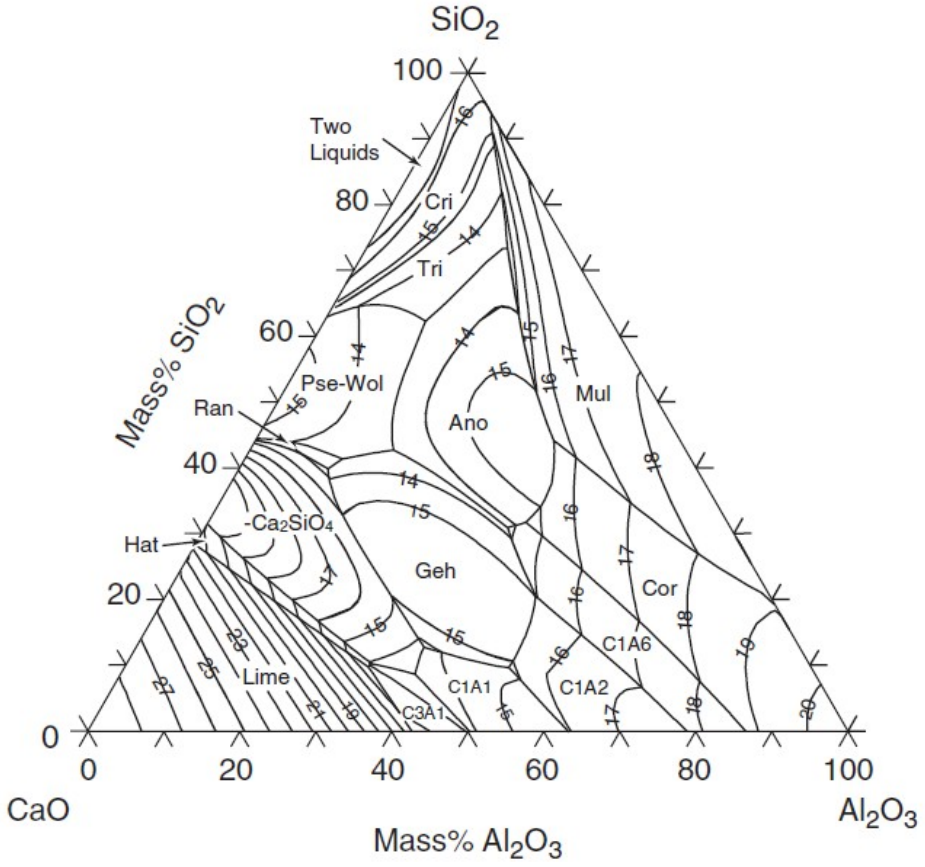
→ $p = x(Si\text{-}Si) / Y(SiO_2)$

Use binomial distribution to calculate Q^n

$Y(Q^4) = p^4$; $Y(Q^3) = 4p^3(1-p)$; $Y(Q^2) = 6p^2(1-p)_2$
$Y(Q^1) = 4p(1-p)^3$; $Y(Q^0) = (1-p)^4$



Ionic liquid model



$(Ca^{+2},Al^{+3})_p(AlO_2^{-1},O^{-2},SiO_4^{-4},SiO_2^{0})_q$

Pure SiO_2 : SiO_2^{0}

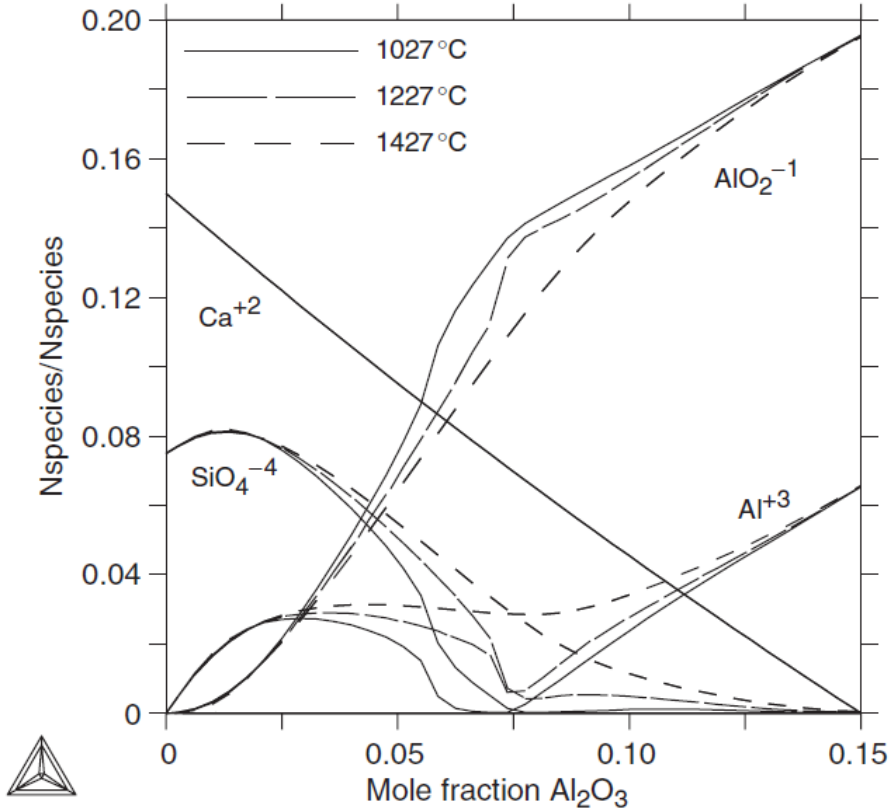
Pure CaO : $(Ca^{+2})_1(O^{-2})_1$

Pure Al_2O_3 : $(Al^{+3})_p(AlO_2^{-1},O^{-2})_q$

$(Al^{+3})_2(O^{-2})_3$

$(Al^{+3})_1(AlO_2^{-1})_3$

Ionic liquid model



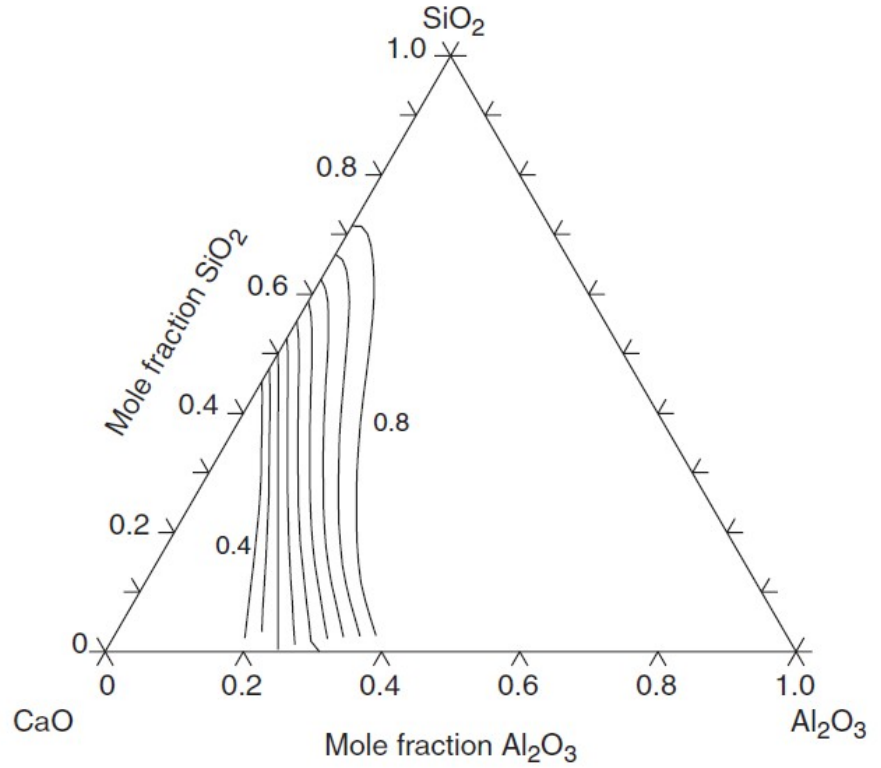
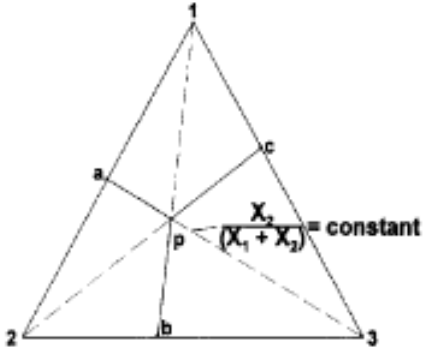
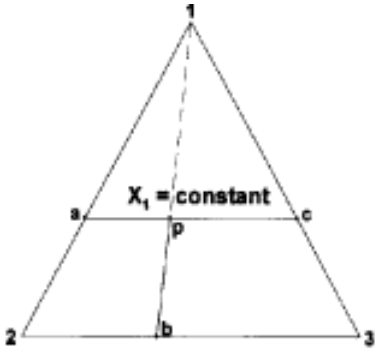


Fig. 14. Calculated iso-concentration lines for the amount of $y_{SiO_2^0} + y_{AlO_2^{-1}}$, between 0.4 and 0.8, with a 0.05 interval at 1900°C.

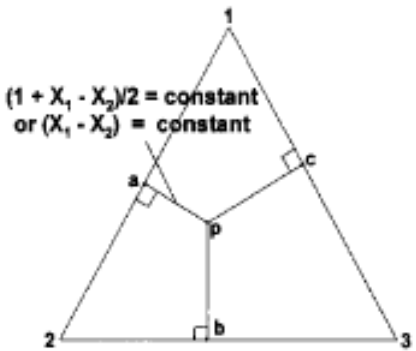
Calphad modeling: Higher order extrapolation



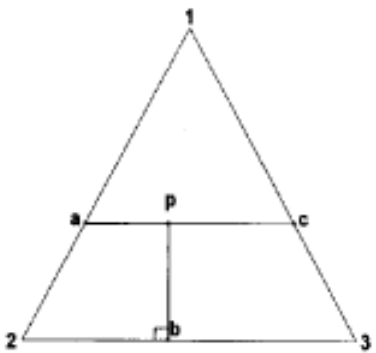
(a) Kohler Model [1]



(b) Kohler / Toop Model [2]



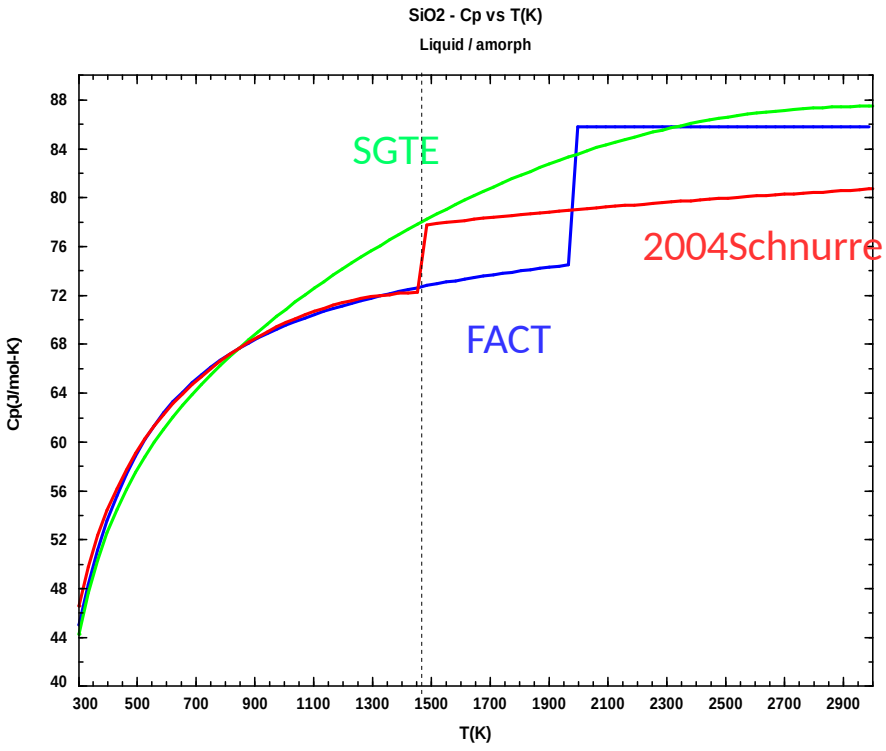
(c) Muggianu Model [3]

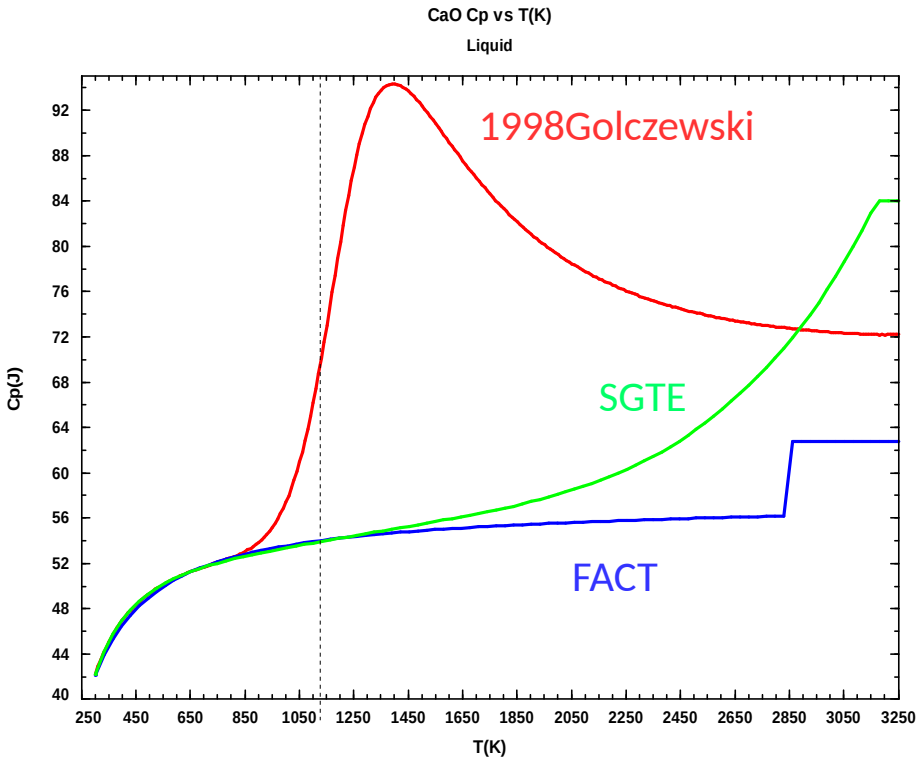


(d) Muggianu /Toop Model [4]

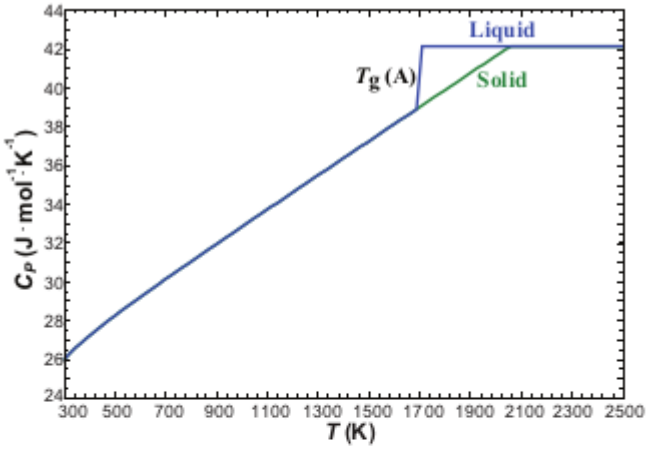
Extrapolation of binary systems into ternary and higher order systems

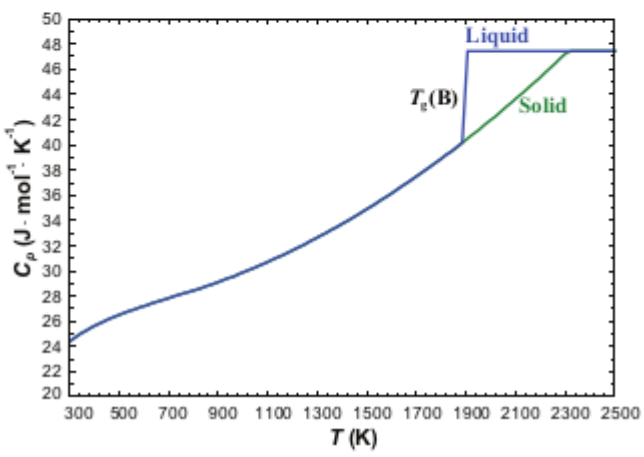
What about the glass transition ?

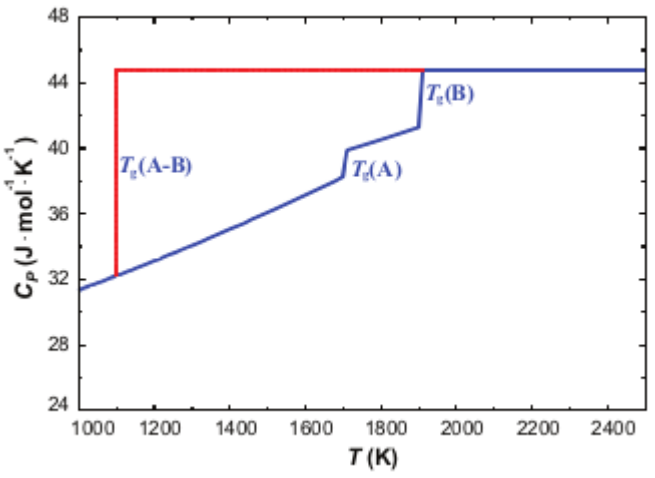




What about the glass transition ?







Two-state model

Atoms are either “solid-like” or “liquid-like” and the Gibbs energy difference between the two is ΔG^{d}_{m}

$$\Delta G^{d}_{m} = G^{liq}_{m} - G^{sol}_{m} = H^{liq}_{m} - H^{sol}_{m} - RT + \cdots,$$

The Gibbs energy for the liquid phase at any given temperature becomes

$$G^{L}_{m} = G^{sol}_{m} + \chi \Delta G^{d}_{m} + RT((1-\chi)\ln(1-\chi) + \chi \ln \chi).$$

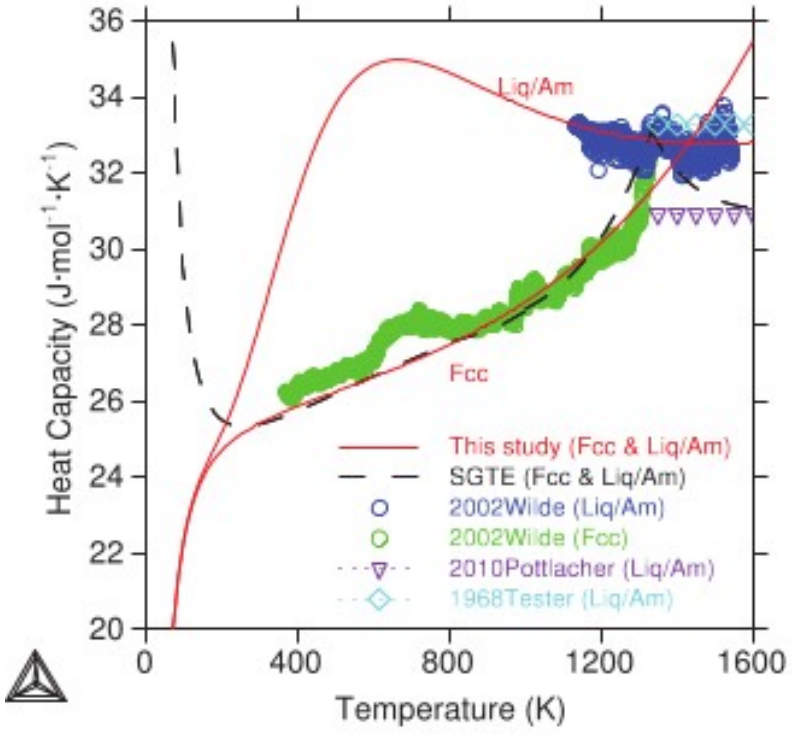
χ is an internal order parameter and can be solved analytically by calculating $\partial Gm/\partial \chi = 0$

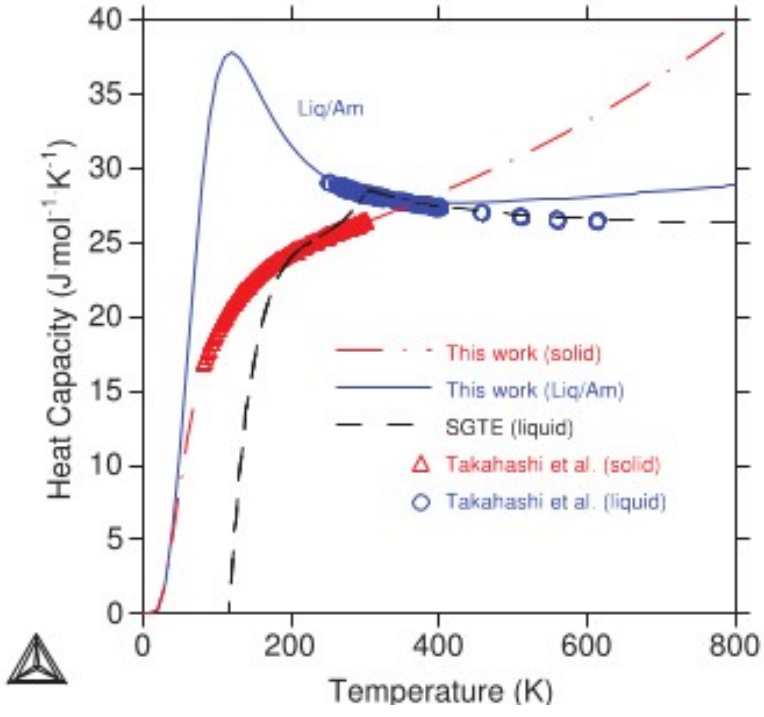
$$\chi = \frac{\exp(-\Delta G^{d}_{m}/RT)}{1+\exp(-\Delta G^{d}_{m}/RT)}.$$

The Gibbs energy for the liquid phase becomes

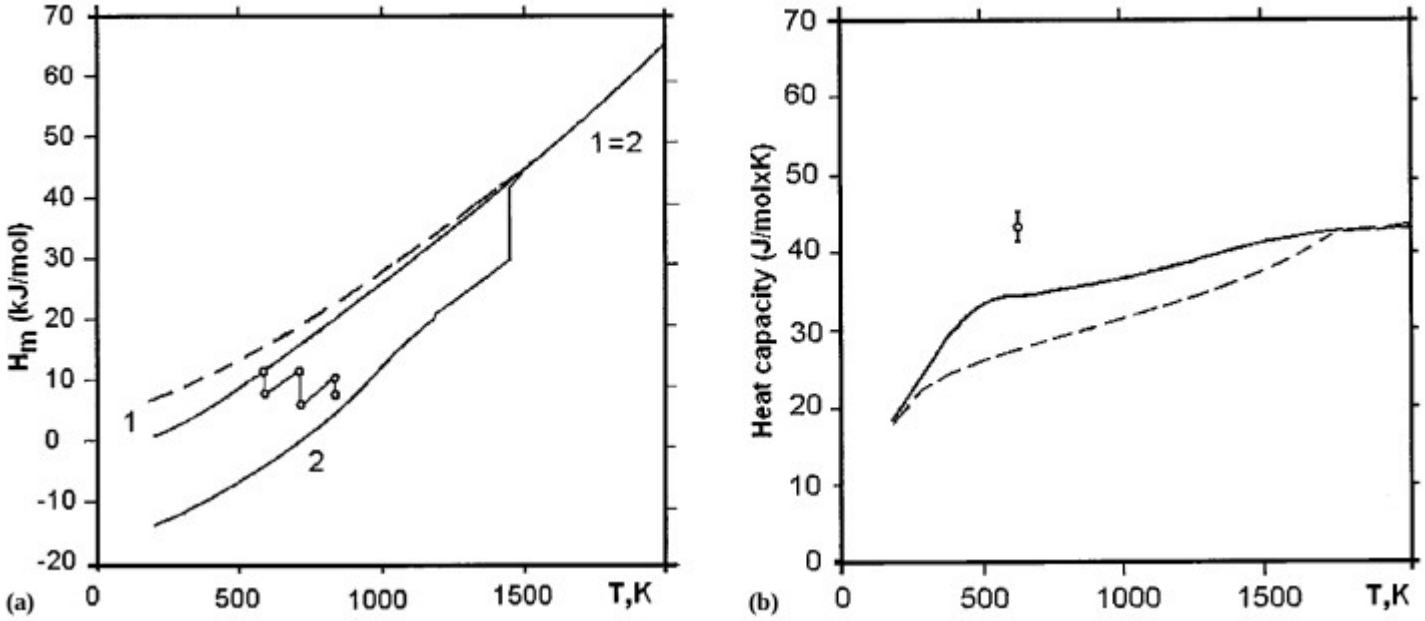
$$G^{L}_{m} = G^{sol}_{m} - RT \ln\left(1+\exp\left(\frac{-\Delta G^{d}_{m}}{RT}\right)\right).$$

Two-state model





Two-state model



$Fe_{85}B_{15}$ amorphous sample : dotted line SGTE, solid Two-state

Conclusions

- The Calphad method allows to model the thermodynamic properties of the liquid/amorphous phase
- Three different thermodynamic models are currently applied to model short range order
  - Associate model (Q-species)
  - Quasi-chemical model (bonding)
  - Ionic liquid model
- Structural features of the liquid are generally well reproduced
- Modeling of the glass transition is still a challenge
  - Two state model is promising, but only applied to elements / binary metallic systems
- Large databases are available commercially
  - >20 elements for metallic systems
  - >10 components for oxides systems