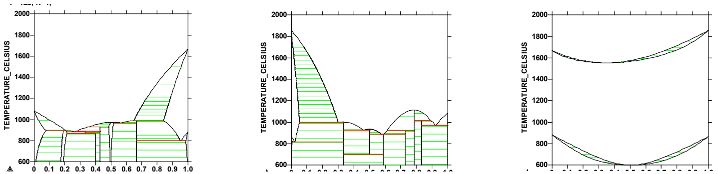
FS 2025/26

MSE-422 – Advanced Metallurgy

10 – Thermodynamic and kinetic modeling

Christian Leinenbach

The CALPHAD approach



optimised A-B

optimised A-C

optimised B-C

extrapolated A-B-C

key experimental data estimation

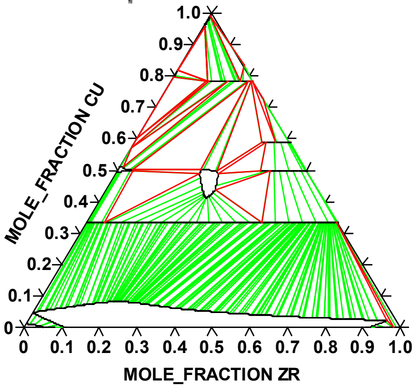
optimised A-B-C

$$G = \underline{\sum x_i G_i^0} + \underline{R\,T\; x_i \ln x_i} + \underline{G^{ex}}$$

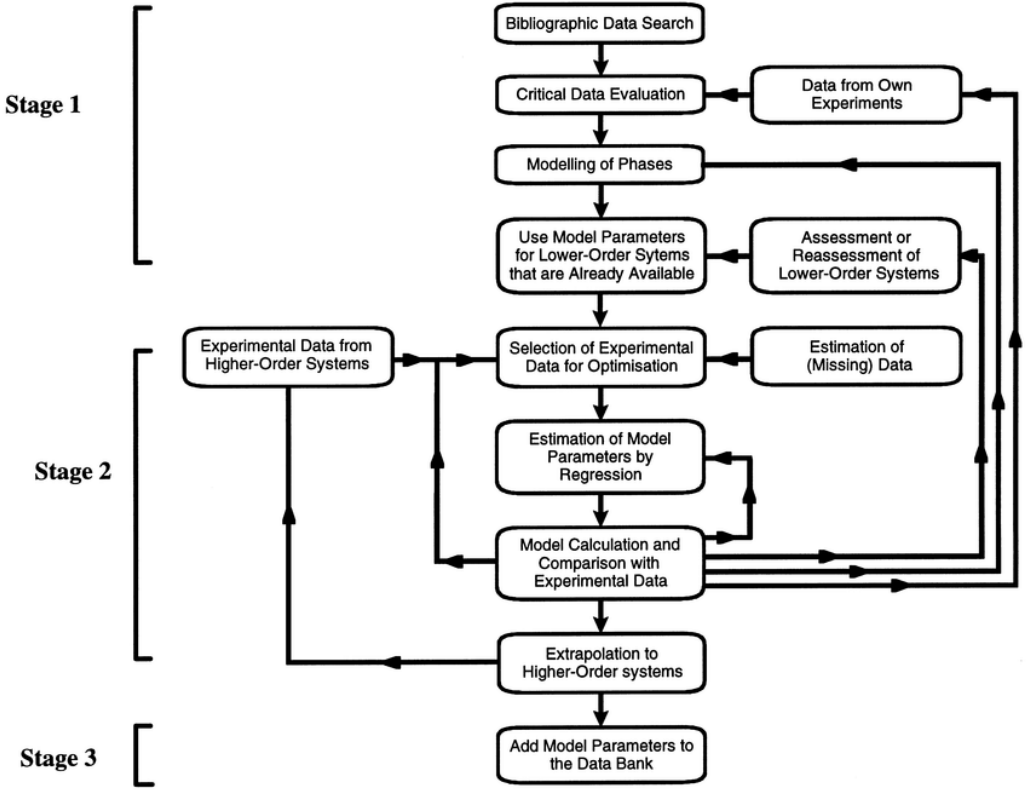
Binary Assessment: $\underline{G^{ex}_{bin}}$

Extrapolation $(\sum G^{ex}_{bin})$

Ternary + Assessment: $\underline{G^{ex}_{ter}}$



CALPHAD flowchart



Thermodynamic modeling

- The CALPHAD method is based on the thermodynamic modeling of solution phases and stoichiometric compunds
- For all solution phases, the Gibbs energy G must be determined

$$G = G^0 + G_m^{ideal} + G_m^{ex} + G_m^{phys}$$

Contribution of pure elements

Ideal mixing contribution

Contribution due to non-ideal interactions

physical contribution (e.g. magnetic)

- Solution phase = solid solution (e.g. FCC, BCC, HCP….) or LIQUID
- Thermodynamic modeling implies the mathematical description of each phase, thereby considering the physical properties of the phase (e.g. lattice structure, Cp, etc.) as precisely as possible

Thermodynamic modeling

Pure elements

- The integral Gibbs energy of a pure element φ in the state i (neglecting p) is

$$G_i^{\varphi}(T) = H - TS$$

- Considering the definitions of H and S this can be written as

$$G_i^{\varphi}(T) = H_m^{SER} + \int_0^T C_p dT - T\int_0^T \frac{C_p}{T} dT$$

with H_m^{SER}: enthalpy of the element/substance in its defined reference state at 298.15K and 1bar

- In the case of elements, the functions recommended by Scientific Group Thermodata Europe (SGTE) are generally used for representing G_i^{φ}:

$${}^0G_i^{\varphi}(T) = G_i^{\varphi}(T) - H_m^{SER} = a + bT + cTln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$$

Where a, b, c are the model parameters

- For ferromagnetic substances, a magnetical ordering term G_{mag}^{φ} needs to be added:

$$G_{mag}^{\varphi}(T) = RTln(1+\beta)g(\tau)$$

where $\tau = T/T_C$, T_C is the critical temperature for magnetic transition, β is the magnetic moment in Bohr magneton and *g(τ)* is the magnetic ordering function

Thermodynamic modeling

Stoichiometric compounds

- The same approach can be extended to model the Gibbs energy function of a stoichiometric compound θ

$$G_i^{\theta}(T) = \sum_i \nu_i H_i^{SER} + A + BT + CTln(T) + DT^2 + \cdots$$

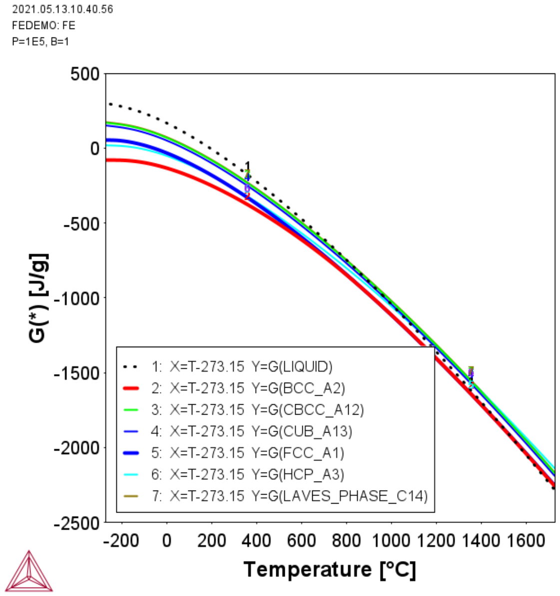
where A, B, C. . . are the model parameters and ν_i are the stoichiometric coefficients for the elements that make up the compound

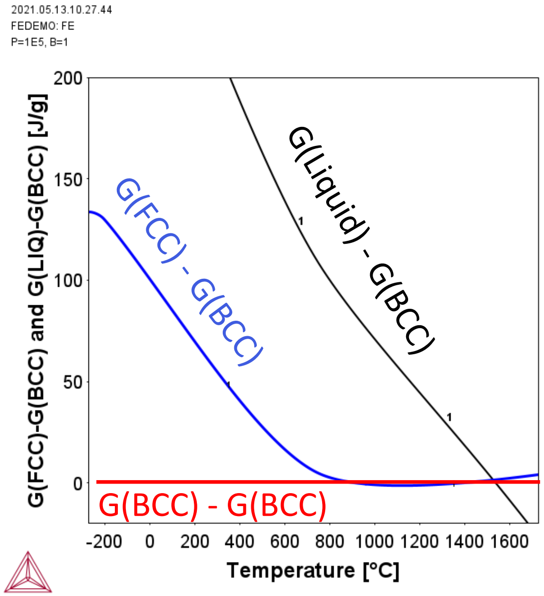
- For compounds with zero C_p of formation or where C_p is not known, a simpler expression can be used

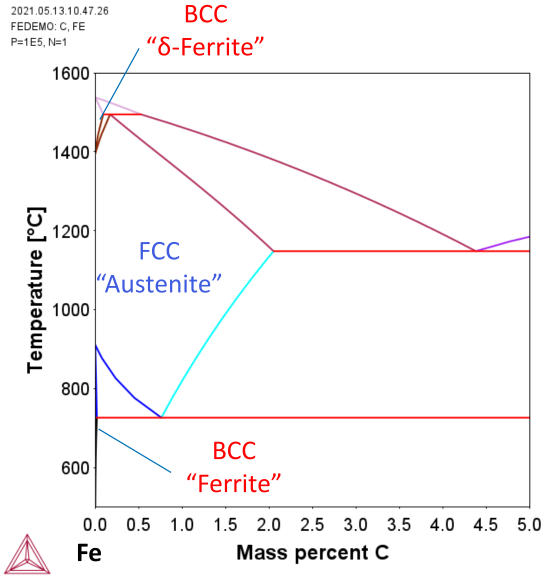
$$G_i^{\theta}(T) = \sum_i \nu_i G_i^{ref} + \Delta_f H^{\theta} - T\Delta_f S^{\theta} = \sum_i \nu_i G_i^{ref} + I + JT$$

Thermodynamic modeling

Example: Gibbs energies of phases in pure iron





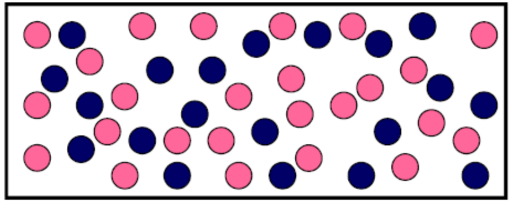


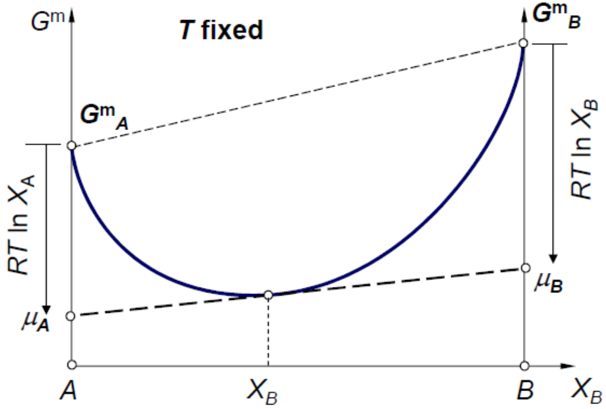
Thermodynamic modeling

Ideal solutions

- The simplest model for binary solutions is the ideal solution model
- It can readily be extended to solutions of higher order (more components)
- Its assumptions are that
  - the distribution of the atoms A and B is completely random
  - the exchange energy between atoms of type A and B is equal to the average exchange energy of A-A bonds and B-B bonds.

$$G_m^\alpha = \sum_i x_i G_i^0 + RT \sum_i x_i ln x_i$$





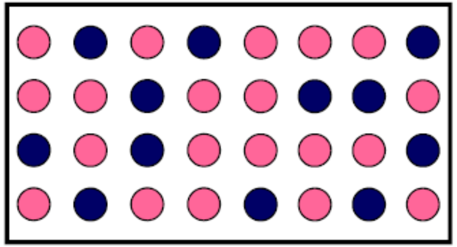
Thermodynamic modeling

Regular solutions

- In regular solutions the exchange energy in A-B bonds is no longer equal to the average of the bond energies of A-A and B-B bonds.
- A mixing enthalpy $\Delta H_{mix} = \Omega X_A X_B$ needs to be added
- Ω is a (temperature dependent) parameter that describes the interaction between A and B atoms

$$\Omega = N_a z\left(\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)\right)$$

N_a: Avogrado constant
z: coordination number



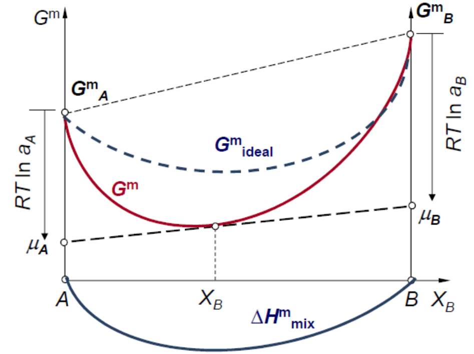
$$G_m^{\alpha} = \sum_i x_i G_i^0 + RT\sum_i x_i ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij}$$

- Depending on the type of bonds, Ω<0 (A and B “like” each other) or Ω>0 (A and B “dislike” each other)

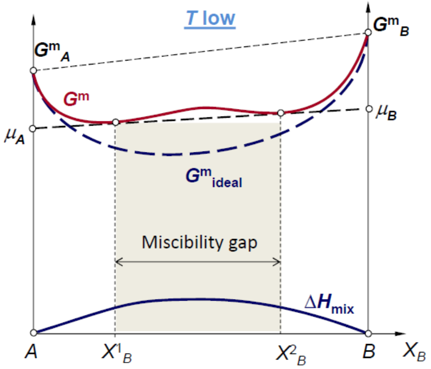
Thermodynamic modeling

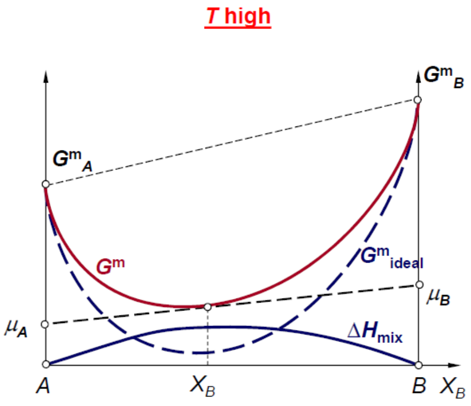
Regular solutions

- Case $\Omega<0$: A and B “like” each other
  - G_m remains concave at any temperature and the enthalpy of mixing only reinforces the “attractiveness” of A and B atoms.



- Case $\Omega>0$: A and B “dislike” each other
  - At high temperature, $-T\Delta S_m$ still dominates and G_m remains concave. At lower temperature, the enthalpy of mixing dominates and can lead to demixing (miscibility gap).





Thermodynamic modeling

Real solutions

- Real solutions deviate to variable extent from ideal or regular solutions. The reason for this can be that
  1) The exchange energy of A-B bonds is not independent of the composition (no unique Ω);
  2) The interaction between atoms of different type leads to a preferential arrangement of atoms A-B (instead of a random arrangement)
  3) Atoms can only take certain positions in a crystal or the liquid (e.g. for topological (size) or chemical reasons)
- These aspects are considered in
  1) The $(\text{sub})^n$-regular solution model (no physics, just numerical)
  2) The sub-lattice model
  3) The quasi-chemical approach

Thermodynamic modeling

Real solutions – the (sub)^n-regular solution model

- A numerical approach that facilitates the calculation of phase diagrams is the Redlich-Kister formalism
- The enthalpy of mixing is not necessarily symmetric and higher order terms allow introducing some degree of skewedness to the enthalpy of mixing curve
- The Gibbs free energy is give as

$$G_m^{\alpha} = \sum_i x_i G_i^0 + RT \sum_i x_i ln x_i + \sum_i \sum_{j>i} x_i x_j \sum_k L_{ij}^k \left(x_i - x_i\right)^k$$

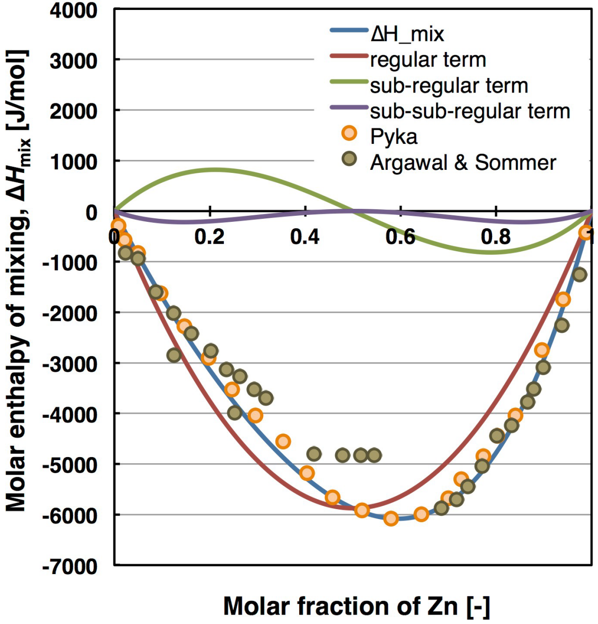
Where L_{ij}^k is a binary interaction parameter dependent on the value of k; L_{ij}^k=A_k+B_kT+C_kTlnT+…

- Examples for binary alloys of A and B
  - Regular solution: $L_{AB}^0 \neq 0, L_{AB}^k \ (k \geq 1) = 0$
  - Sub-regular solution: $L_{AB}^0, L_{AB}^1 \neq 0, L_{AB}^k \ (k \geq 2) = 0$
  - Sub-sub-regular solution: $L_{AB}^0, L_{AB}^1, L_{AB}^2 \neq 0, L_{AB}^k \ (k \geq 3) = 0$
- In some cases higher order interaction might not be neglected and a ternary interaction parameter is introduced: $G_{ABC}^{ex} = x_A x_B x_C L_{ABC}^k$

Thermodynamic modeling

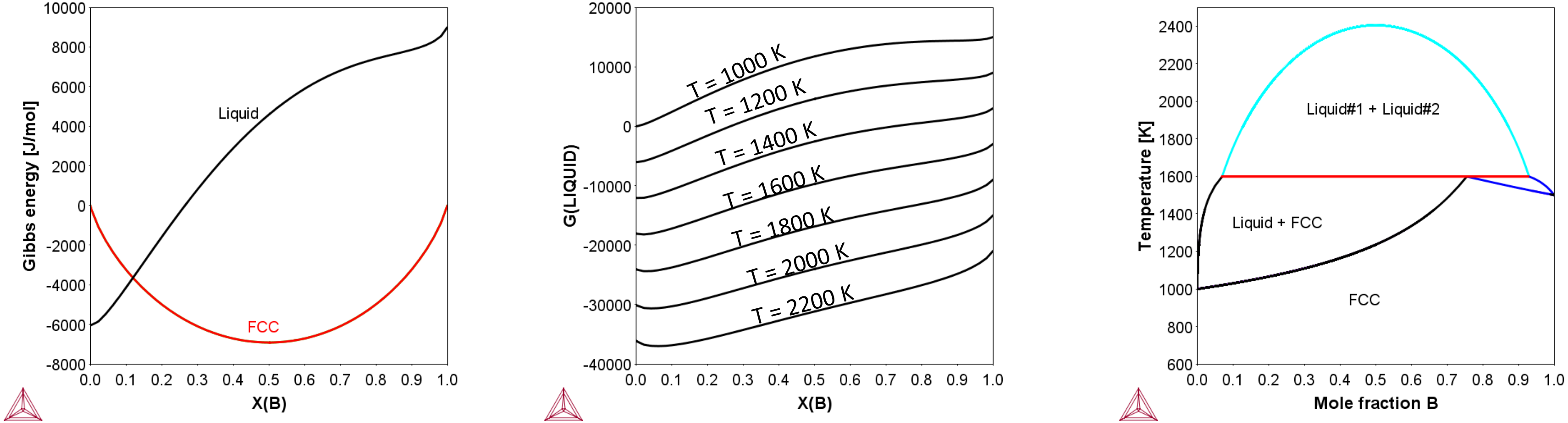
Real solutions – the (sub)^n-regular solution model

- The sub-regular solution model is used for substitutional phases such as liquid, bcc, fcc, etc.
- It cannot be used for interstitial solutions, ordered intermetallics or ceramic compounds
- There is little evidence for the need of interaction parameters of any higher order than 2
- Prediction of thermodynamic properties of substitutional phases is based on binary and ternary terms
- Example: enthalpy of mixing of liquid Mg-Zn
  - experimental data from calorimetry measurements
  - Data fitting leads to
    $L^0_{Mg-Zn,liq}$= -23500 kJ/mol
    $L^1_{Mg-Zn,liq}$= 8500 kJ/mol
    $L^2_{Mg-Zn,liq}$= -3500 kJ/mol



Thermodynamic modeling

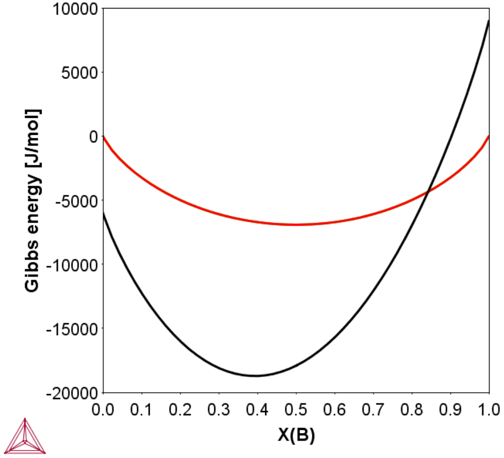
Example: influence of interaction parameters on phase stabilities

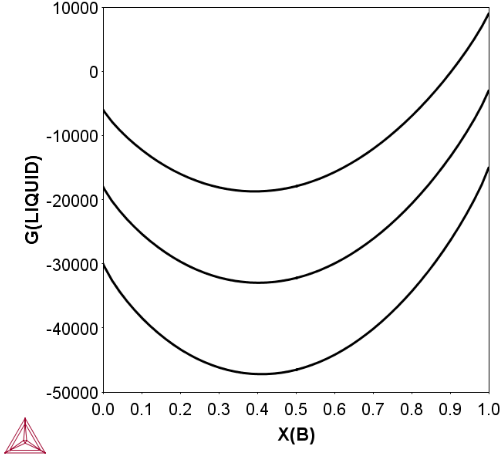


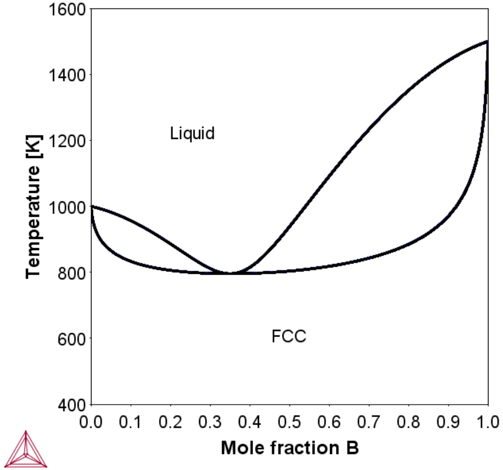
$$G_m^{ex,liquid} = x_A x_B \, {}^{0}L_{A,B} = x_A x_B \cdot (+40000)$$ → **negative excess term**

Thermodynamic modeling

Example: influence of interaction parameters on phase stabilities







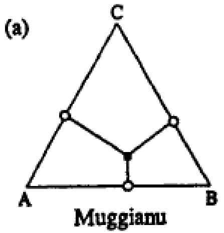
$$G_m^{ex,liquid} = x_A x_B \; {}^{0}L_{A,B} = x_A x_B \cdot (-50000)$$ → **negative excess term**

Thermodynamic modeling

Real solutions – extrapolation to higher order systems

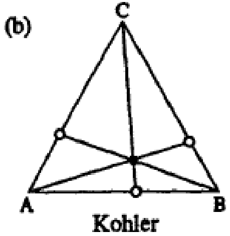
- Extrapolation of thermodynamic properties of alloys into multi-component systems is based on the summation of the binary and ternary excess parameters
- The formulae for doing this are based on various geometrical weightings of the mole fractions
- Muggianu’s model:

$$G^{ex}_{mix,ABC} = x_A x_B\{L^0_{AB} + L^1_{AB}(x_A - x_B)\}$$
$$+x_B x_C\{L^0_{BC} + L^1_{BC}(x_B - x_C)\}$$
$$+x_A x_C\{L^0_{AC} + L^1_{AC}(x_A - x_C)\}$$



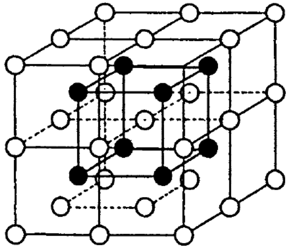
- Kohler’s model:

$$G^{ex}_{mix,ABC} = (x_A - x_B)^2 \frac{x_A}{x_A + x_B} \cdot \frac{x_B}{x_A + x_B} \left\{L^0_{AB} + L^1_{AB}\left(\frac{x_A - x_B}{x_A + x_B}\right)\right\}$$
$$+(x_B - x_C)^2 \frac{x_B}{x_B + x_C} \cdot \frac{x_C}{x_B + x_C} \left\{L^0_{BC} + L^1_{BC}\left(\frac{x_B - x_C}{x_B + x_C}\right)\right\}$$
$$+(x_A - x_C)^2 \frac{x_A}{x_A + x_C} \cdot \frac{x_C}{x_A + x_C} \left\{L^0_{AC} + L^1_{AC}\left(\frac{x_A - x_C}{x_A + x_C}\right)\right\}$$



Thermodynamic modeling

Real solutions – the sublattice model



- A sublattice (SL) phase can be considered as being composed of interlocking sublattices on which the various components can mix
- The model is phenomenological in nature and does not necessarily define any crystal structure within its mathematical formulation (but can)
- Consider a phase with N distinct lattice sites, each forming a SL; the fractional site occupation of components on the different sublattices are:

$$y_i^s = \frac{n_i^s}{N^s} \text{ or including vacancies } y_i^s = \frac{n_i^s}{n_{Va}^s + \sum_i n_i^s}$$

Where n_i^s number of atoms of component i on sublattice s; N^s total number of sites on the sublattice

- Mole fractions are related to site fractions according to

$$x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{Va}^s)}$$

- The ideal entropy of mixing is made up of the configurational contributions from mixing on each SL

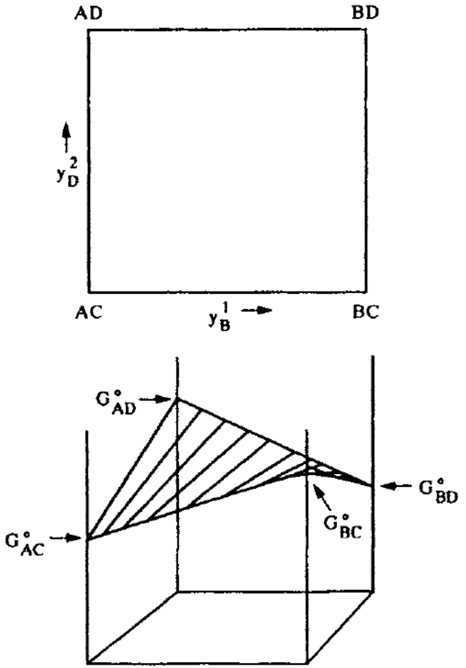
$$G_m^{id} = -TS_m^{id} = RT \sum_s N^s \sum_i y_i^s \ln y_i^s$$

Thermodynamic modeling

Real solutions – the sublattice model

- Consider a sublattice (SL) phase consisting of the elements A, B, C, and D where only A and B will be on the same lattice site and C and D can occupy only another lattice site: $(A,B)_1(C,D)_1$
- It is possible for four points of ‘complete occupation’ to exist where pure A exist on SL1 and either pure C or D on SL2 (or pure B on SL1 and either pure C or D on SL2)
- These four compounds are the ‘end members’, which define the Gibbs energy reference surface.
- The composition of the phase is in the space between the four end members and ist Gibbs energy is given by

$$G_m^{ref} = y_A y_C G_{AC}^0 + y_B y_C G_{BC}^0 + y_A y_D G_{AD}^0 + y_B y_D G_{BD}^0$$



Thermodynamic modeling

Real solutions – the sublattice model

- Consider again the two-SL system $(A,B)_1(C,D)_1$
- The interactions A-C, A-D, B-C, B-D are controlled by the Gibbs energies of the compounds AC, AD, BC and BD
- Mixing on the SLs controls A-B and C-D interactions and

$$G_{mix}^{ex} = y_A^1 y_B^1 L_{A,B:*}^0 + y_C^1 y_D^1 L_{*:C,D}^0$$

- A sub-regular model can be introduced by making the interactions compositionally dependent on the site occupation in the other SL

$$G_{mix}^{ex} = y_A^1 y_B^1 y_C^2 L_{A,B:C}^0 + y_A^1 y_B^1 y_D^2 L_{A,B:D}^0 + y_C^1 y_D^1 y_A^2 L_{A:C,D}^0 + y_C^1 y_D^1 y_B^2 L_{B:C,D}^0$$

- It is possible to add some site fraction dependence to these parameters

  e.g. $L_{A,B:C}^0 = y_A^1 y_B^1 y_C^2 \sum_\nu L_{A,B:C}^\nu \left(y_A^1 - y_B^1\right)^\nu$

Thermodynamic modeling

Applications the sublattice model

- The sublattice model is one of the most predominant methods used to describe solution and compound phases, e.g. for
  - Line compounds in ternary systems
  - Interstitial phases → carbides $(Fe,Cr,Ni,\ldots)_n(C,Va)_m$
  - Complex intermetallic compounds with significant variation in stoichiometry
  - Order-disorder transformations

Thermodynamic modeling

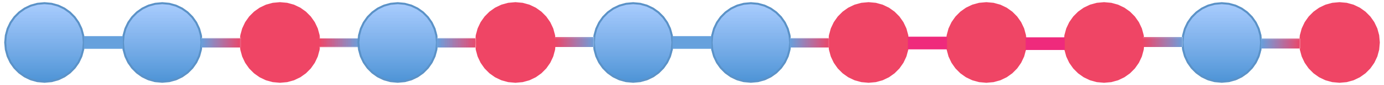
Real solutions – the quasi-chemical approach

- The regular solution model assumes a random distribution of atoms even though the enthalpy of mixing is not zero
- In reality, a random solution is only expected at very high temperatures when the entropy term overwhelms any tendency for ordering or clustering of atomst; the atom arrangement is no longer random and the entropy of mixing, $\Delta^{mix}S$, may differ from the ideal value
- The quasi-chemical approach takes into account that the interactions between atoms A and B are more or less energetic, which leads to preferential formation of A-B bonds ($\Omega<0$) or A-A and B-B bonds ($\Omega>0$)
- The model is so–called because it has a mass–action equation which is typical in chemical reaction theory

Thermodynamic modeling

Real solutions – the quasi-chemical approach

- Consider a binary system A-B of N atoms with the concentration x_A and x_B
- To understand the principle the situation where the atoms are arranged on a 1-dimensional lattice is considered ("Ising"-model)



- The total number of bonds emanating from an atom of type A are $x_A Nz$, with Z the coordination number of an atom (Z=2 in the 1D case)
- Of all the bonds emanating from an atom of type A, bonds of type A-B and of type B-A have to be subtracted (the A-B bonds are not interchangeable with the B-A bonds)
  - Number of A-A bonds: $N_{AA} = \frac{1}{2}(x_A ZN - N_{AB} - N_{BA})$
  - Number of B-B bonds: $N_{BB} = \frac{1}{2}(x_B ZN - N_{AB} - N_{BA})$

Thermodynamic modeling

The quasi-chemical approach – enthalpy term

- The total number of heterogeneous bonds, N_{het}, is $N_{het} = N_{AB} + N_{BA}$ and the number of A-B bonds is equal to the number of B-A bonds: $N_{AB} = N_{BA}$; The total number of bonds is NZ/2
- The concentration of bonds, n_{ik}, of the different types is:

$$\left.\begin{aligned} n_{AB} &= \frac{N_{AB}}{\frac{NZ}{2}} \\ n_{BA} &= \frac{N_{BA}}{\frac{NZ}{2}} \end{aligned}\right\} n_{het} = \frac{N_{AB} + N_{BA}}{\frac{NZ}{2}}$$

$$n_{AA} = \frac{N_{AA}}{\frac{NZ}{2}} = \left(x_A - \frac{1}{2}\frac{N_{AB}}{\frac{NZ}{2}} - \frac{1}{2}\frac{N_{BA}}{\frac{NZ}{2}} \right) = \left(x_A - \frac{1}{2} n_{AB} - \frac{1}{2} n_{BA} \right) = \left(x_A - \frac{n_{het}}{2} \right)$$

$$n_{BB} = \frac{N_{BB}}{\frac{NZ}{2}} = \left(x_B - \frac{1}{2}\frac{N_{AB}}{\frac{NZ}{2}} - \frac{1}{2}\frac{N_{BA}}{\frac{NZ}{2}} \right) = \left(x_B - \frac{1}{2} n_{AB} - \frac{1}{2} n_{BA} \right) = \left(x_B - \frac{n_{het}}{2} \right)$$

- These bonds contribute to the Gibbs free energy by γ_{AA}, γ_{BB}, and γ_{AB} for A-A, B-B, and A-B as well as B-A bonds, respectively. The total Gibbs free energy, G, is then

$$G(N) = \frac{NZ}{2}\left(n_{AA}\gamma_{AA} + n_{het}\gamma_{AB} + n_{BB}\gamma_{BB} \right) - TS_c = \frac{NZ}{2}\left(\left(x_A - \frac{n_{het}}{2} \right)\gamma_{AA} + n_{het}\gamma_{AB} + \left(x_B - \frac{n_{het}}{2} \right)\gamma_{BB} \right) - TS_c$$

$$G(N) = \underbrace{\frac{NZ}{2}\left(x_A\gamma_{AA} + x_B\gamma_{BB} \right)}_{x_A G_A(N) + x_B G_B(N)} + \underbrace{\frac{NZ}{2}\left(n_{het}\left(\gamma_{AB} - \left(\frac{\gamma_{AA} + \gamma_{BB}}{2} \right) \right) \right) - TS_c}_{\Delta^{mix} G(N)}$$

Thermodynamic modeling

The quasi-chemical approach – entropy term

- Assume that there is no contribution to entropy by e.g. change in lattice vibrations due to the A-B bonds $\left(\gamma_{AB} - \frac{\gamma_{AA} + \gamma_{BB}}{2}\right) = \left(\varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right) = \omega$
- The total configurational entropy of the system of bonds, $S_{c,\text{bonds}}$, can be calculated as

$$S_{c,\text{bonds}} = k_B \ln W; \qquad W = \frac{\frac{NZ}{2}!}{N_{AA}!\,N_{BB}!\,\frac{1}{2}N_{AB}!\,\frac{1}{2}N_{AB}!} = \frac{\frac{NZ}{2}!}{\left(n_{AA}\frac{NZ}{2}\right)!\left(n_{BB}\frac{NZ}{2}\right)!\left(n_{AB}\frac{NZ}{2}\right)!\left(n_{BA}\frac{NZ}{2}\right)!}$$

- With Sterling’s formula, i.e. ln(x!) = $x$ln(x), this can be written as:

$$S_{c,\text{bonds}} = k_B\left[\left(\frac{NZ}{2}\right)\ln\left(\frac{NZ}{2}\right) - \left(n_{AA}\frac{NZ}{2}\right)\ln\left(n_{AA}\frac{NZ}{2}\right) - \left(n_{BB}\frac{NZ}{2}\right)\ln\left(n_{BB}\frac{NZ}{2}\right) - \left(n_{AB}\frac{NZ}{2}\right)\ln\left(n_{AB}\frac{NZ}{2}\right) - \left(n_{BA}\frac{NZ}{2}\right)\ln\left(n_{BA}\frac{NZ}{2}\right)\right]$$

$$S_{c,\text{bonds}} = \frac{NZ}{2}k_B\left[\ln\left(\frac{NZ}{2}\right) - n_{AA}\ln\left(n_{AA}\frac{NZ}{2}\right) - n_{BB}\ln\left(n_{BB}\frac{NZ}{2}\right) - n_{AB}\ln\left(n_{AB}\frac{NZ}{2}\right) - n_{BA}\ln\left(n_{BA}\frac{NZ}{2}\right)\right]$$

$$S_{c,\text{bonds}} = \frac{NZ}{2}k_B\left[\ln\left(\frac{NZ}{2}\right) - n_{AA}\left(\ln(n_{AA}) + \ln\left(\frac{NZ}{2}\right)\right) - n_{BB}\left(\ln(n_{BB}) + \ln\left(\frac{NZ}{2}\right)\right) - n_{AB}\left(\ln(n_{AB}) + \ln\left(\frac{NZ}{2}\right)\right) - n_{BA}\left(\ln(n_{BA}) + \ln\left(\frac{NZ}{2}\right)\right)\right]$$

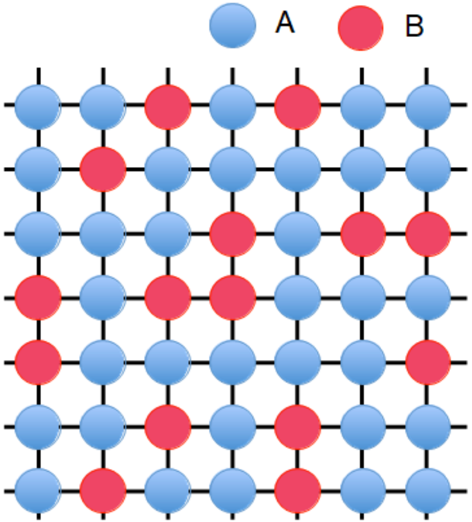
$$S_{c,\text{bonds}} = \frac{NZ}{2}k_B\left[\ln\left(\frac{NZ}{2}\right)(1 - n_{AA} - n_{BB} - n_{AB} - n_{BA}) - n_{AA}\ln(n_{AA}) - n_{BB}\ln(n_{BB}) - n_{AB}\ln(n_{AB}) - n_{BA}\ln(n_{BA})\right]$$

$$S_{c,\text{bonds}} = -\frac{NZ}{2}k_B\left[n_{AA}\ln(n_{AA}) + n_{BB}\ln(n_{BB}) + n_{AB}\ln(n_{AB}) + n_{BA}\ln(n_{BA})\right]$$

Thermodynamic modeling

The quasi-chemical approach

- In calculating the configurational entropy of the bond system, it was considered that A-B bonds, A-A bonds, B-B bonds, and B-A bonds are permutable amongst themselves
- However, A-B bonds are different from B-A bonds (not in their energy but with regard to permutability)
- It was assumed that the bonds can be placed randomly on the lattice of bonds, but there are already some restrictions on the Ising chain model
  - e.g. an A-A bond cannot be next to a B-B bond, neither can an A-B bond be to the left of a A-A bond (but a A-A bond or a B-A bond can).
- The arrangement of the bonds is hence somehow restricted (→ 2D model)
- Accounting for this in a 3D network of bonds in a detailed way becomes awfully complicated



Thermodynamic modeling

The quasi-chemical approach

- The entropy cannot be larger than in a fully random arrangement of the atoms.
- For 1 mole (i.e. N = Na) of a binary mixture of atoms, the maximum configurational entropy is attained when xA = xB = 0.5 and Sc,atoms = RZln(2)
- If we do the same calculation for the bonds, again for 1 mole of atoms, the maximum is obtained when nAA = nBB = nAB = nBA = 0.25, and its value is sc,bonds = RZln(4)/2
- It cannot be that the configurational entropy changes just because we looked at another entity, i.e. bonds rather than atoms
- the entropy calculated for the bonds can be normalized with regard the one obtained for the atoms by looking at their respective maximum value and assuming that also outside the maximum with the normalization factor Φ

$$\Phi = \frac{S_{c,atoms}}{S_{c,bonds}} = \frac{2ln(2)}{Zln(4)} = \frac{1}{Z}$$

- The molar Gibbs free energy of mixing Gmix, as a function of the bond concentration of heterogenous bonds

Thermodynamic modeling

The quasi-chemical approach

- The molar Gibbs free energy of mixing G_{mix}, as a function of the bond concentration of heterogenous bonds becomes

$$\Delta^{mix} g = \frac{N_a Z}{2} n_{het}\omega + T\frac{N_a Z}{2}\Phi k_B \left[\underbrace{\left(x_A - \frac{n_{het}}{2}\right)}_{n_{AA}} \ln \underbrace{\left(x_A - \frac{n_{het}}{2}\right)}_{n_{AA}} + \underbrace{\left(x_B - \frac{n_{het}}{2}\right)}_{n_{BB}} \ln \underbrace{\left(x_B - \frac{n_{het}}{2}\right)}_{n_{BB}} + \underbrace{\frac{n_{het}}{2}}_{n_{AB}} \ln \underbrace{\left(\frac{n_{het}}{2}\right)}_{n_{AB}} + \underbrace{\frac{n_{het}}{2}}_{n_{BA}} \ln \underbrace{\left(\frac{n_{het}}{2}\right)}_{n_{BA}} \right]$$

- The equilibrium value for the bond concentration n_{het} is found when G_{mix} is minimum
- Setting the 1st derivative 0, rearranging and considering $\Phi=1/Z$

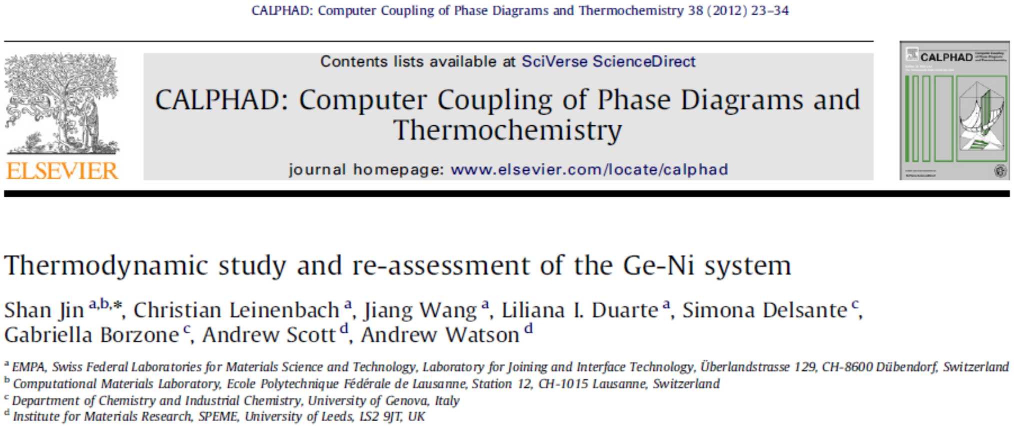
$$TR\left[ln\left(x_A - \frac{n_{het}}{2}\right) + ln\left(x_B - \frac{n_{het}}{2}\right) - 2ln\left(\frac{n_{het}}{2}\right)\right] = 2N_A Z\omega$$

with $N_A Z\omega = \Omega$: $$exp\left(\frac{2\Omega}{RT}\right) = \frac{\left(x_A - \frac{n_{het}}{2}\right)\left(x_B - \frac{n_{het}}{2}\right)}{2\left(\frac{n_{het}}{2}\right)} = \frac{[n_{AA}][n_{BB}]}{[n_{AB}][n_{BA}]}$$

Looks like mass-action:

Thermodynamic modeling

Example: assessment of the binary Ge-Ni system



CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 38 (2012) 23–34

Contents lists available at SciVerse ScienceDirect

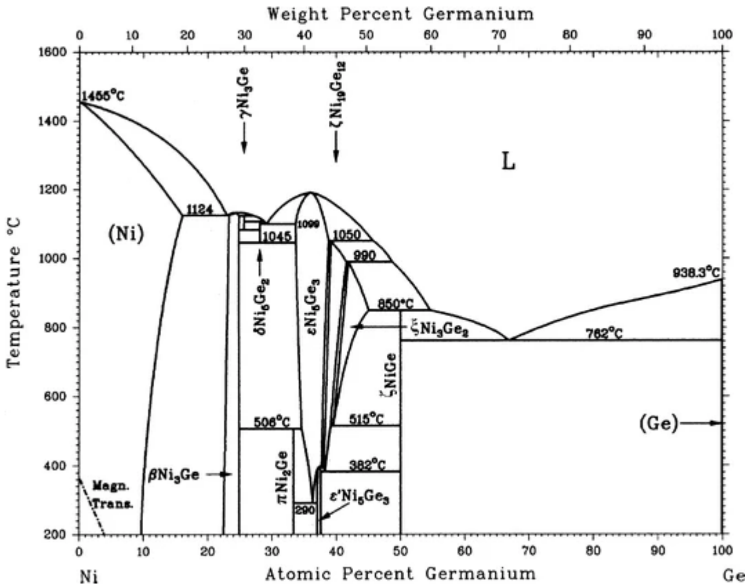
CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Thermodynamic study and re-assessment of the Ge-Ni system

Shan Jin[a,b,*], Christian Leinenbach[a], Jiang Wang[a], Liliana I. Duarte[a], Simona Delsante[c], Gabriella Borzone[c], Andrew Scott[d], Andrew Watson[d]

[a] EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining and Interface Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
[b] Computational Materials Laboratory, Ecole Polytechnique Fédérale de Lausanne, Station 12, CH-1015 Lausanne, Switzerland
[c] Department of Chemistry and Industrial Chemistry, University of Genova, Italy
[d] Institute for Materials Research, SPEME, University of Leeds, LS2 9JT, UK



Thermodynamic modeling

Example: assessment of the binary Ge-Ni system

- Work flow for thermodynamic assessment
  - Review of literature data
  - Own measurements (phase diagram, calorimetry)
  - Thermodynamic modeling
    - Modeling of pure elements $^{0}G_i^{\varphi}(T) = G_i^{\varphi}(T) - H_i^{SER} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$
    - Modeling of solution phases $G_m^{\varphi} = \sum x_i {}^{0}G_i^{\varphi} + RT\sum x_i \ln(x_i) + {}^{E}G_m^{\varphi} + {}^{mag}G_m^{\varphi}$

$$^{E}G_m^{\varphi} = x_{Ge}x_{Ni}\sum_{j=0}^{n} {}^{(j)}L_{Ge,Ni}^{\varphi}(x_{Ge} - x_{Ni}) \qquad {}^{(j)}L_{Ge,Ni}^{\varphi} = A_j + B_jT + C_jT\ln T \qquad {}^{\text{mag}}G_m^{\varphi} = RT\ln(\beta^{\varphi} + 1)f(\tau^{\varphi})$$

-
  -
    - Modeling of ordered phases $G_m = G_m^{disord}(x_i) + G_m^{ord}(y_i', y_i'') - G_m^{ord}(x_i)$
    - Modeling of B8-type non-stoichiometric compound Ni_5Ge_3 → 3-sublattice model (Ge)(Ni)(Va,Ni)

$$^{0}G_{Ge:Ni:Va}^{Ni_5Ge_3} = {}^{0}G_{Ge}^{DIAMOND\_A4} + {}^{0}G_{Ni}^{FCC\_A1} + E + FT$$

$$^{0}G_{Ge:Ni:Ni}^{Ni_5Ge_3} = {}^{0}G_{Ge}^{DIAMOND\_A4} + 2\,{}^{0}G_{Ni}^{FCC\_A1} + E' + F'T$$

$$G_m^{Ni_5Ge_3} = y_{Va}^{III}\,{}^{0}G_{Ge:Ni:Va}^{Ni_5Ge_3} + y_{Ni}^{III}\,{}^{0}G_{Ge:Ni:Ni}^{Ni_5Ge_3} + RT(y_{Ni}^{III}\ln y_{Ni}^{III} + y_{Va}^{III}\ln y_{Va}^{III}) + {}^{E}G_m^{Ni_5Ge_3}$$

$$^{E}G_m^{Ni_5Ge_3} = y_{Va}^{III}y_{Ni}^{III}L_{Ge:Ni:Va,Ni}^{Ni_5Ge_3} \qquad L_{Ge:Ni:Va,Ni}^{Ni_5Ge_3} = \sum_{n=0}(G_n + H_nT)(y_{Ni}^{III} - y_{Va}^{III})^n$$

-
  -
    - Modeling of stoichiometric phases

$$G_m^{NiGe} = 0.5\,{}^{0}G_{Ni}^{FCC\_A1} + 0.5\,{}^{0}G_{Ge}^{DIAMOND\_A4} + a + b + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7$$

$$G_m^{Ni_xGe_y} = \frac{x}{x+y}\,{}^{0}G_{Ni}^{FCC\_A1} + \frac{y}{x+y}\,{}^{0}G_{Ge}^{DIAMOND\_A4} + I_{Ni_xGe_y} + J_{Ni_xGe_y}T$$

Thermodynamic modeling

Example: assessment of the binary Ge-Ni system

- Work flow for thermodynamic assessment
  - Parameter optimization (→ least-square fitting algorithm in Thermo-Calc)

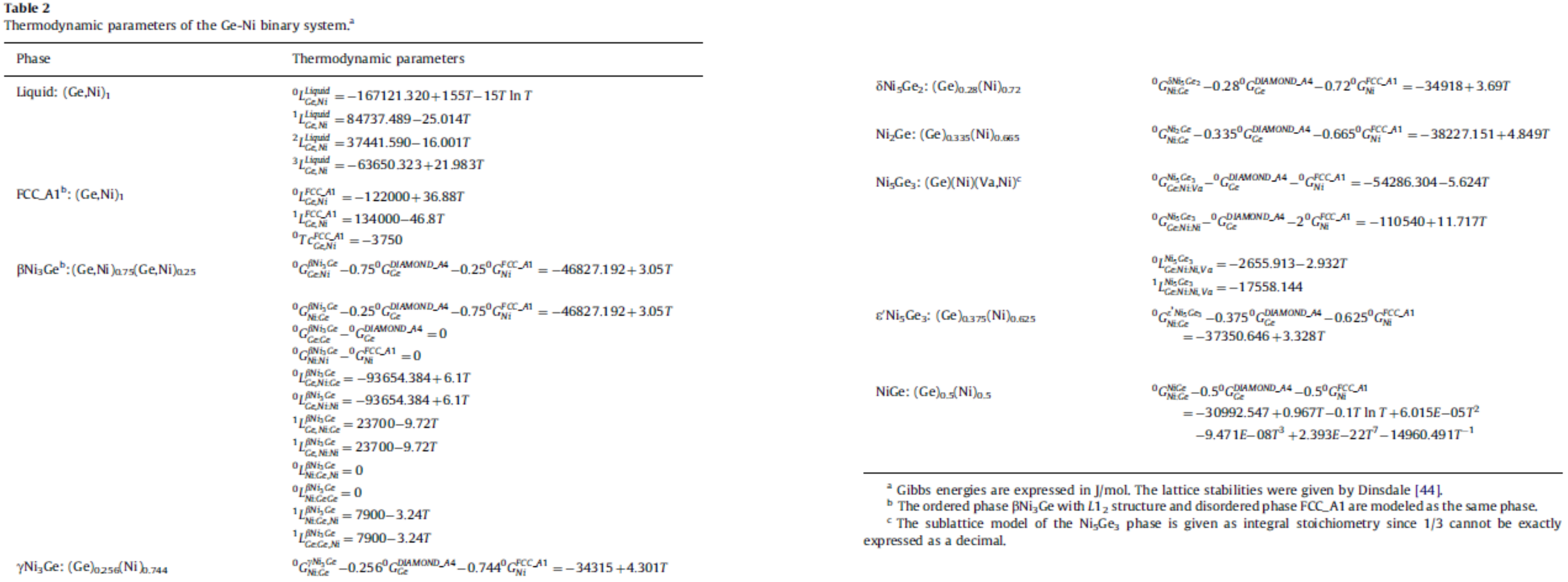


Table 2
Thermodynamic parameters of the Ge-Ni binary system.[a]

Phase	Thermodynamic parameters
Liquid: $(Ge,Ni)_1$	${}^{0}L^{Liquid}_{Ge,Ni} = -167121.320 + 155T - 15T \ln T$ ${}^{1}L^{Liquid}_{Ge,Ni} = 84737.489 - 25.014T$ ${}^{2}L^{Liquid}_{Ge,Ni} = 37441.590 - 16.001T$ ${}^{3}L^{Liquid}_{Ge,Ni} = -63650.323 + 21.983T$
FCC_A1[b]: $(Ge,Ni)_1$	${}^{0}L^{FCC\_A1}_{Ge,Ni} = -122000 + 36.88T$ ${}^{1}L^{FCC\_A1}_{Ge,Ni} = 134000 - 46.8T$ ${}^{0}Tc^{FCC\_A1}_{Ge,Ni} = -3750$
βNi_3Ge[b]: $(Ge,Ni)_{0.75}(Ge,Ni)_{0.25}$	${}^{0}G^{\beta Ni_3Ge}_{Ge:Ni} - 0.75\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.25\,{}^{0}G^{FCC\_A1}_{Ni} = -46827.192 + 3.05T$ ${}^{0}G^{\beta Ni_3Ge}_{Ni:Ge} - 0.25\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.75\,{}^{0}G^{FCC\_A1}_{Ni} = -46827.192 + 3.05T$ ${}^{0}G^{\beta Ni_3Ge}_{Ge:Ge} - {}^{0}G^{DIAMOND\_A4}_{Ge} = 0$ ${}^{0}G^{\beta Ni_3Ge}_{Ni:Ni} - {}^{0}G^{FCC\_A1}_{Ni} = 0$ ${}^{0}L^{\beta Ni_3Ge}_{Ge,Ni:Ge} = -93654.384 + 6.1T$ ${}^{0}L^{\beta Ni_3Ge}_{Ge,Ni:Ni} = -93654.384 + 6.1T$ ${}^{1}L^{\beta Ni_3Ge}_{Ge,Ni:Ge} = 23700 - 9.72T$ ${}^{1}L^{\beta Ni_3Ge}_{Ge,Ni:Ni} = 23700 - 9.72T$ ${}^{0}L^{\beta Ni_3Ge}_{Ni:Ge,Ni} = 0$ ${}^{0}L^{\beta Ni_3Ge}_{Ni:GeGe} = 0$ ${}^{1}L^{\beta Ni_3Ge}_{Ni:Ge,Ni} = 7900 - 3.24T$ ${}^{1}L^{\beta Ni_3Ge}_{Ge:Ge,Ni} = 7900 - 3.24T$
γNi_3Ge: $(Ge)_{0.256}(Ni)_{0.744}$	${}^{0}G^{\gamma Ni_3Ge}_{Ni:Ge} - 0.256\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.744\,{}^{0}G^{FCC\_A1}_{Ni} = -34315 + 4.301T$
δNi_5Ge_2: $(Ge)_{0.28}(Ni)_{0.72}$	${}^{0}G^{\delta Ni_5Ge_2}_{Ni:Ge} - 0.28\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.72\,{}^{0}G^{FCC\_A1}_{Ni} = -34918 + 3.69T$
Ni_2Ge: $(Ge)_{0.335}(Ni)_{0.665}$	${}^{0}G^{Ni_2Ge}_{Ni:Ge} - 0.335\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.665\,{}^{0}G^{FCC\_A1}_{Ni} = -38227.151 + 4.849T$
Ni_5Ge_3: (Ge)(Ni)(Va,Ni)[c]	${}^{0}G^{Ni_5Ge_3}_{Ge:Ni:Va} - {}^{0}G^{DIAMOND\_A4}_{Ge} - {}^{0}G^{FCC\_A1}_{Ni} = -54286.304 - 5.624T$ ${}^{0}G^{Ni_5Ge_3}_{Ge:Ni:Ni} - {}^{0}G^{DIAMOND\_A4}_{Ge} - 2\,{}^{0}G^{FCC\_A1}_{Ni} = -110540 + 11.717T$ ${}^{0}L^{Ni_5Ge_3}_{Ge:Ni:Ni,Va} = -2655.913 - 2.932T$ ${}^{1}L^{Ni_5Ge_3}_{Ge:Ni:Ni,Va} = -17558.144$
$\varepsilon' Ni_5Ge_3$: $(Ge)_{0.375}(Ni)_{0.625}$	${}^{0}G^{\varepsilon' Ni_5Ge_3}_{Ni:Ge} - 0.375\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.625\,{}^{0}G^{FCC\_A1}_{Ni}$ $= -37350.646 + 3.328T$
NiGe: $(Ge)_{0.5}(Ni)_{0.5}$	${}^{0}G^{NiGe}_{Ni:Ge} - 0.5\,{}^{0}G^{DIAMOND\_A4}_{Ge} - 0.5\,{}^{0}G^{FCC\_A1}_{Ni}$ $= -30992.547 + 0.967T - 0.1T \ln T + 6.015E{-}05T^2$ $-9.471E{-}08T^3 + 2.393E{-}22T^7 - 14960.491T^{-1}$

---

[a] Gibbs energies are expressed in J/mol. The lattice stabilities were given by Dinsdale [44].

[b] The ordered phase βNi_3Ge with $L1_2$ structure and disordered phase FCC_A1 are modeled as the same phase.

[c] The sublattice model of the Ni_5Ge_3 phase is given as integral stoichiometry since 1/3 cannot be exactly expressed as a decimal.

Thermodynamic modeling

Example: assessment of the binary Ge-Ni system

- Work flow for thermodynamic assessment
  - Comparison simulation vs experimental data

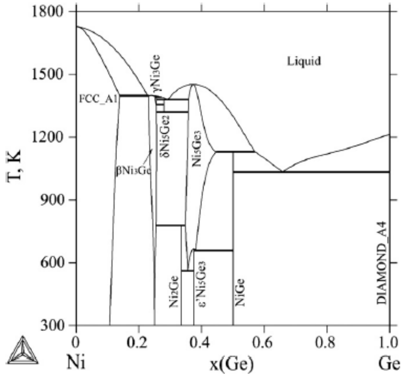


Fig. 4. Calculated phase diagram of the Ge-Ni binary system from the present work.

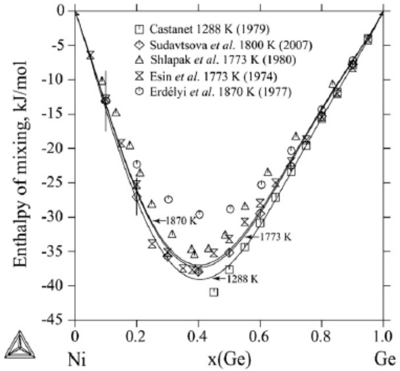


Fig. 6. Calculated enthalpy of mixing of liquid alloys compared with experimental data. (Ref. states: liquid Ge and liquid Ni).

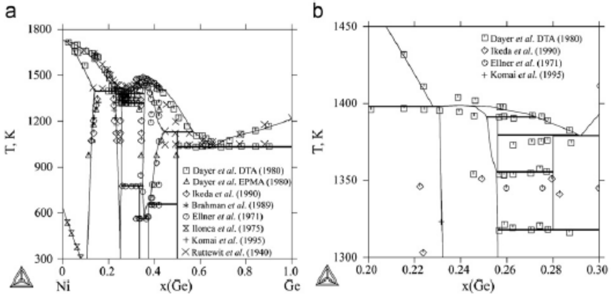


Fig. 5. (a) Calculated phase diagram of the Ge-Ni binary system compared with experimental data. (b) Ni-rich part of the phase diagram compared with experimental data.

Thermodynamic modeling

Example: assessment of the binary Ge-Ni system

- Work flow for thermodynamic assessment
    - Comparison simulation vs experimental data

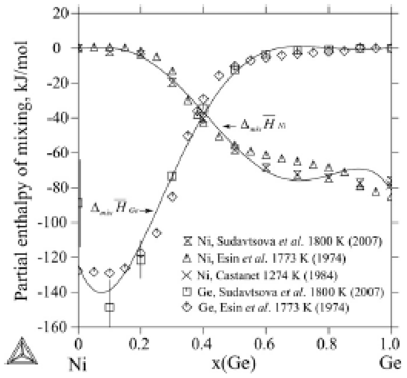


Fig. 7. Calculated partial enthalpy of Ni and Ge in liquid alloys at 1800 K compared with experimental data. (Ref. states: liquid Ge and liquid Ni).

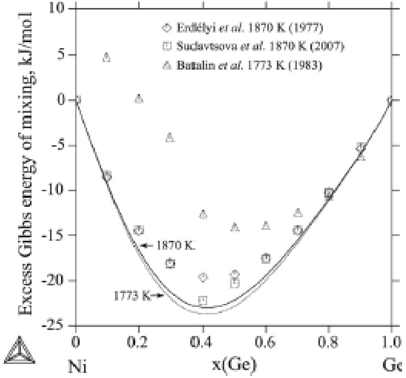


Fig. 9. Calculated excess Gibbs energy of mixing of liquid alloys compared wit experimental data. (Ref. states: liquid Ge and liquid Ni).

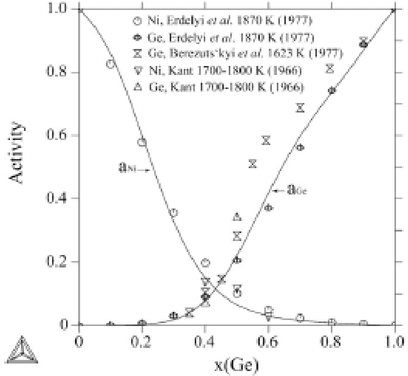


Fig. 8. Calculated activity of Ge and Ni in the Ge-Ni melt at 1870 K compared with experimental data. (Ref. states: liquid Ge and liquid Ni).

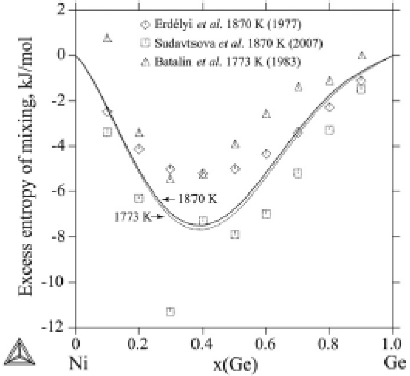
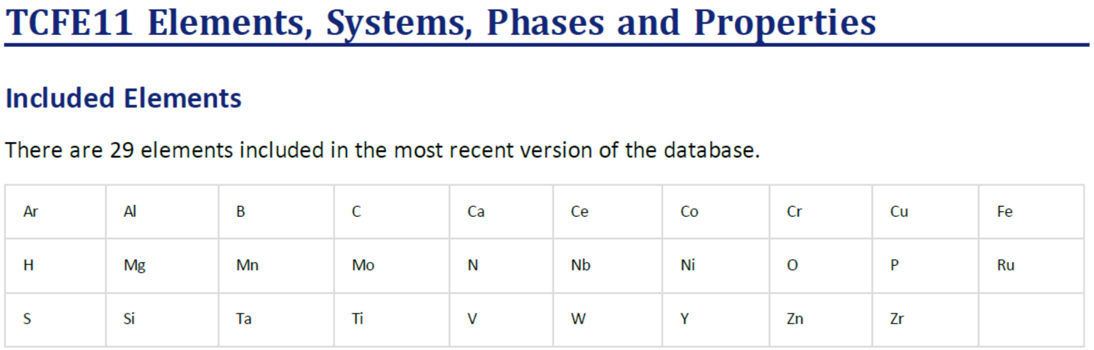


Fig. 10. Calculated excess entropy of mixing of liquid alloys compared with experimental data. (Ref. states: liquid Ge and liquid Ni).

Thermodynamic databases

Steel and Fe-alloys



TCFE11 Elements, Systems, Phases and Properties

Included Elements

There are 29 elements included in the most recent version of the database.

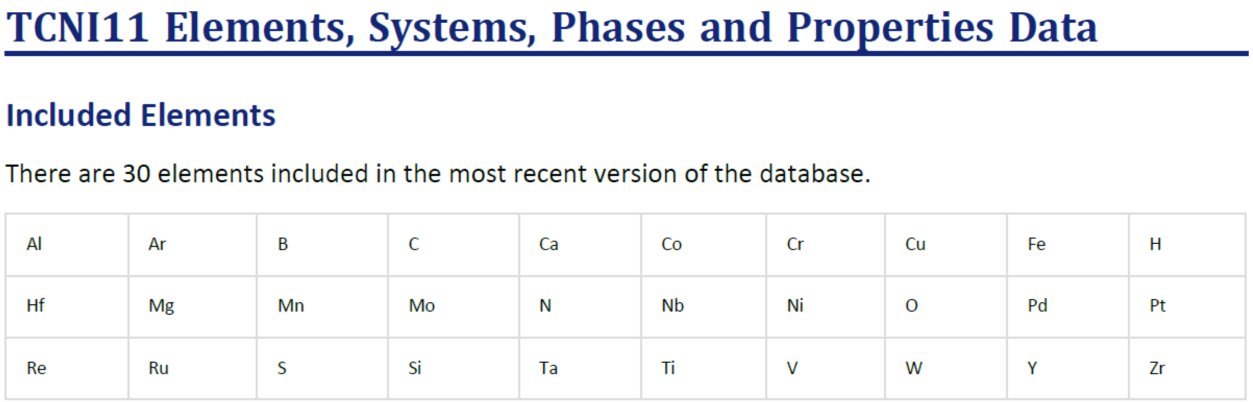
Ar	Al	B	C	Ca	Ce	Co	Cr	Cu	Fe
H	Mg	Mn	Mo	N	Nb	Ni	O	P	Ru
S	Si	Ta	Ti	V	W	Y	Zn	Zr	

The most recent version of the database contains the following:

- 345 assessed binary systems
- 290 assessed ternary systems
- 79 assessed quaternary systems
- Several assessed quinary systems

Thermodynamic databases

Steel and Fe-alloys



TCNI11 Elements, Systems, Phases and Properties Data

Included Elements

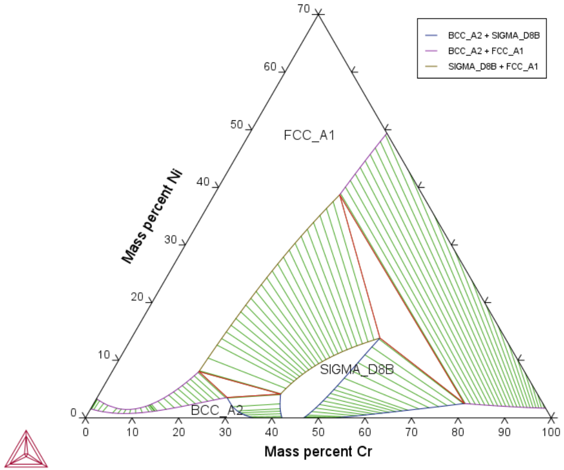
There are 30 elements included in the most recent version of the database.

Al	Ar	B	C	Ca	Co	Cr	Cu	Fe	H
Hf	Mg	Mn	Mo	N	Nb	Ni	O	Pd	Pt
Re	Ru	S	Si	Ta	Ti	V	W	Y	Zr

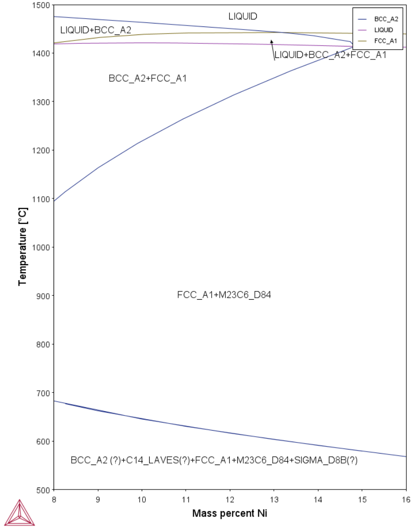
Non-equilibrium transformations

- Thermodynamic simulation software tools allow calculating phase equilibria in multi-component systems as well as equilibrium thermodynamic properties, i.e. complete diffusion in the liquid and solid states are assumed

Fe-Ni-Cr/800°C



X5CrNiMo18-12-3, influence of Ni

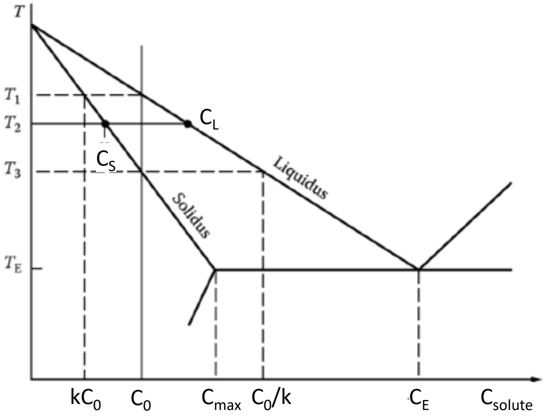


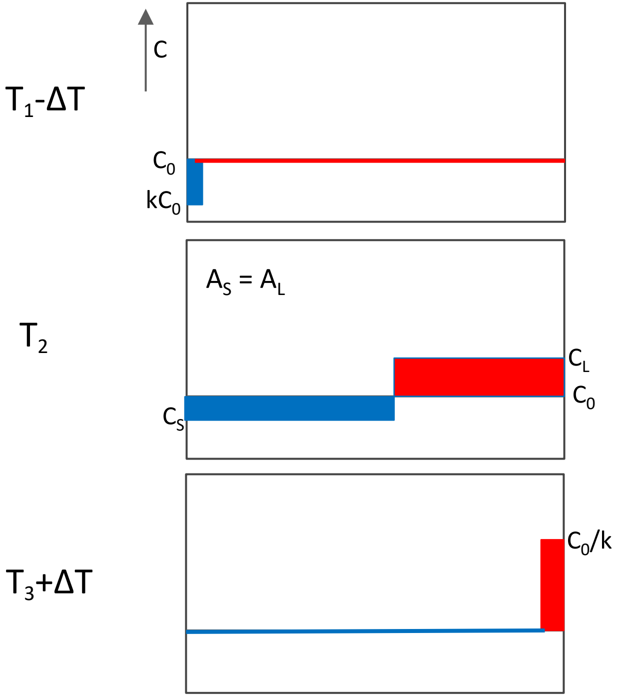
Non-equilibrium transformations

- Thermodynamic simulation software tools allow calculating phase equilibria in multi-component systems as well as equilibrium thermodynamic properties, i.e. complete diffusion in the liquid and solid states are assumed
- Metals processing includes many non-equilibrium steps
  - casting & soldification
  - Solutionizing/homogenization heat treatments
  - Quenching and precipitation hardening
  - Joining (soldering/brazing, diffusion bonding)
- During service of high-performance alloys, diffusion-controlled processes can take place
  - Grain coarsening
  - Precipitate growth
  - Formation of intermetallic compounds at interfaces
- How can these non-equilibrium and time-dependent processes be modeled and simulated?

The equilibrium solidification model

- Under equilibrium conditions, the solidification path in an alloy is given by the lever rule
- The equilibrium solute concentrations are
  - $kC_0 \leq C_S \leq C_0$
  - $C_0 \leq C_L \leq C_0/k < X_E$





The Scheil-Gulliver solidification model

- In reality, solidification typically occurs under non-equilibrium conditions, i.e. the cooling rate is too high to allow time for complete redistribution of alloying elements according to equilibrium
- A qualitative description of the solute redistribution during solidification processes is possible with the so-called “Scheil–Gulliver” model, which was first formulated in 1913 by Gulliver.
- The basic assumptions of the model are:
  - Diffusion of all elements in the liquid phase is infinitely fast
  - Diffusion of all elements in the solid phases is zero
  - The liquid/solid interface is in thermodynamic equilibrium

The Scheil-Gulliver solidification model

- The corresponding differential equation for the mass balance between solid and liquid was presented by Scheil in 1942:

$$(C_L - C_S)df_s = (f_L)dC_L$$

where C_S is the local composition of the solid, C_L of the liquid, f_S is the fraction of solid and f_L is the fraction of liquid

- With the partioning coefficient $k = C_S/C_L$ and considering that mass is conserved $(f_L + f_s = 1)$, the mass balance may be rewritten as

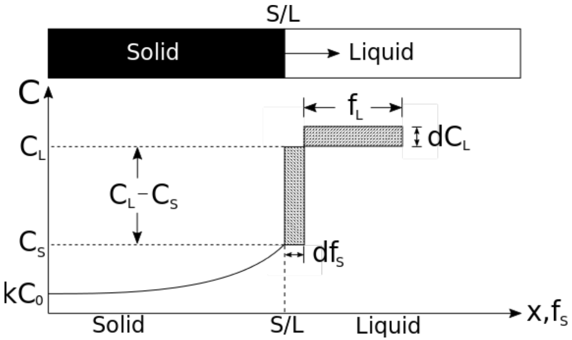
$$C_L(1-k)df_s = (1-f_s)dC_L$$

- Using the boundary condition $C_L = C_0$ at $f_s = 0$

$$\int_0^{f_S} \frac{df_s}{1-f_s} = \frac{1}{1-k}\int_{C_0}^{C_L} \frac{dC_L}{C_L}$$

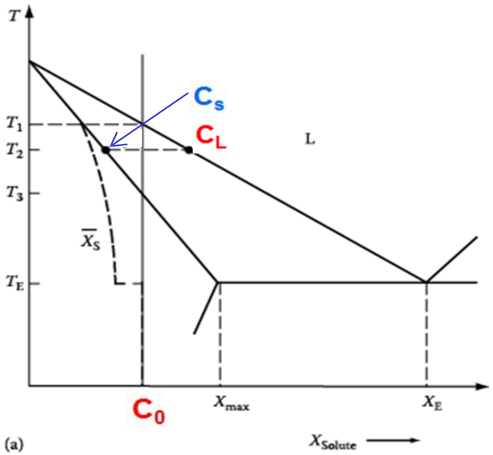
- Integrating results in the Scheil-Gulliver equation for composition of the liquid/solid during solidification gives

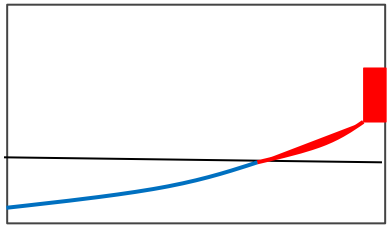
$$C_L = C_0(f_L)^{k-1}; C_s = kC_0(1-f_S)^{k-1}$$



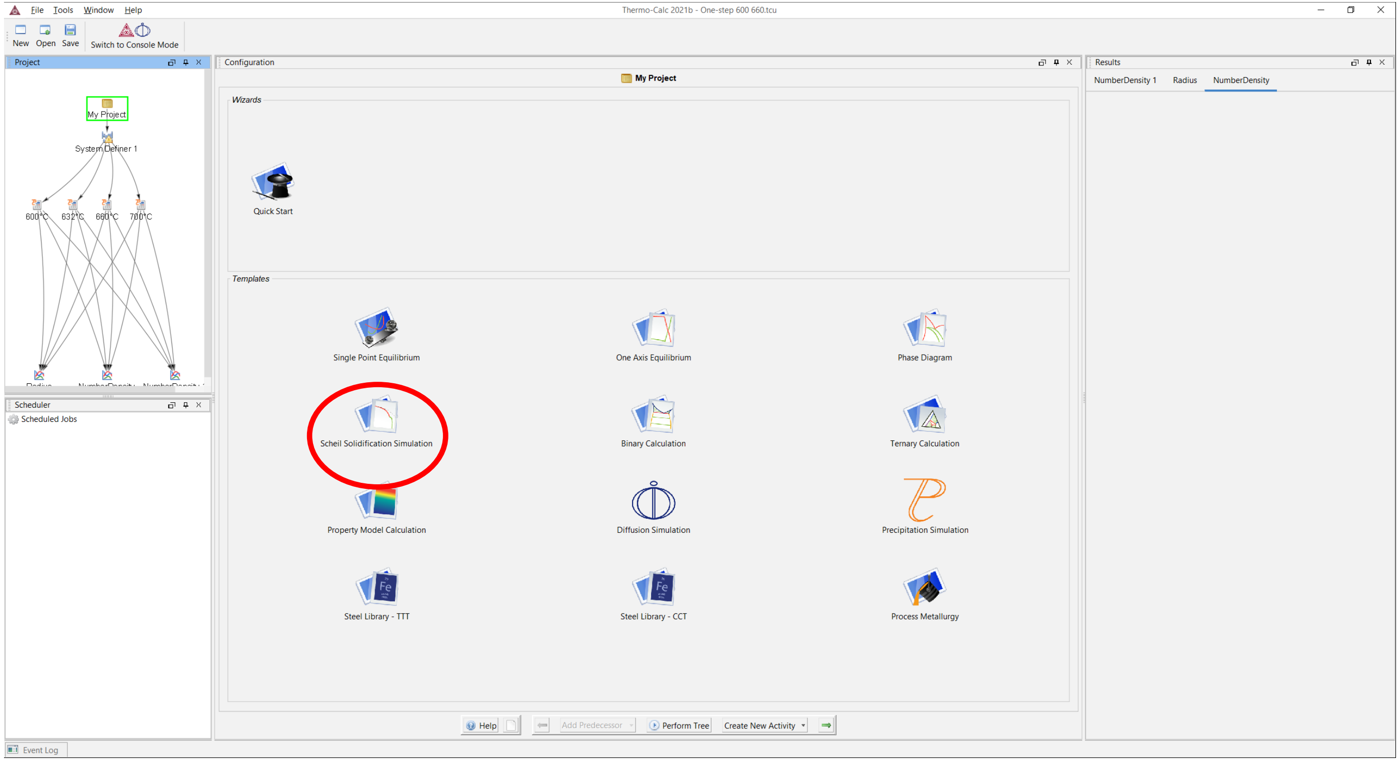
The Scheil-Gulliver solidification model

- Because of complete diffusion in the liquid, the liquid composition is always uniform, although this uniform composition changes as solidification continues
- The composition of the solid varies continuously as the solidification front advances and the solid retains this compositional variation after the front has passed
- The composition of the solid deviates from the equilibrium composition
- Solidification continues down to the eutectic temperature; when TE is reached, the remaining liquid will have the eutectic composition, and it solidifies to form a eutectic solid.

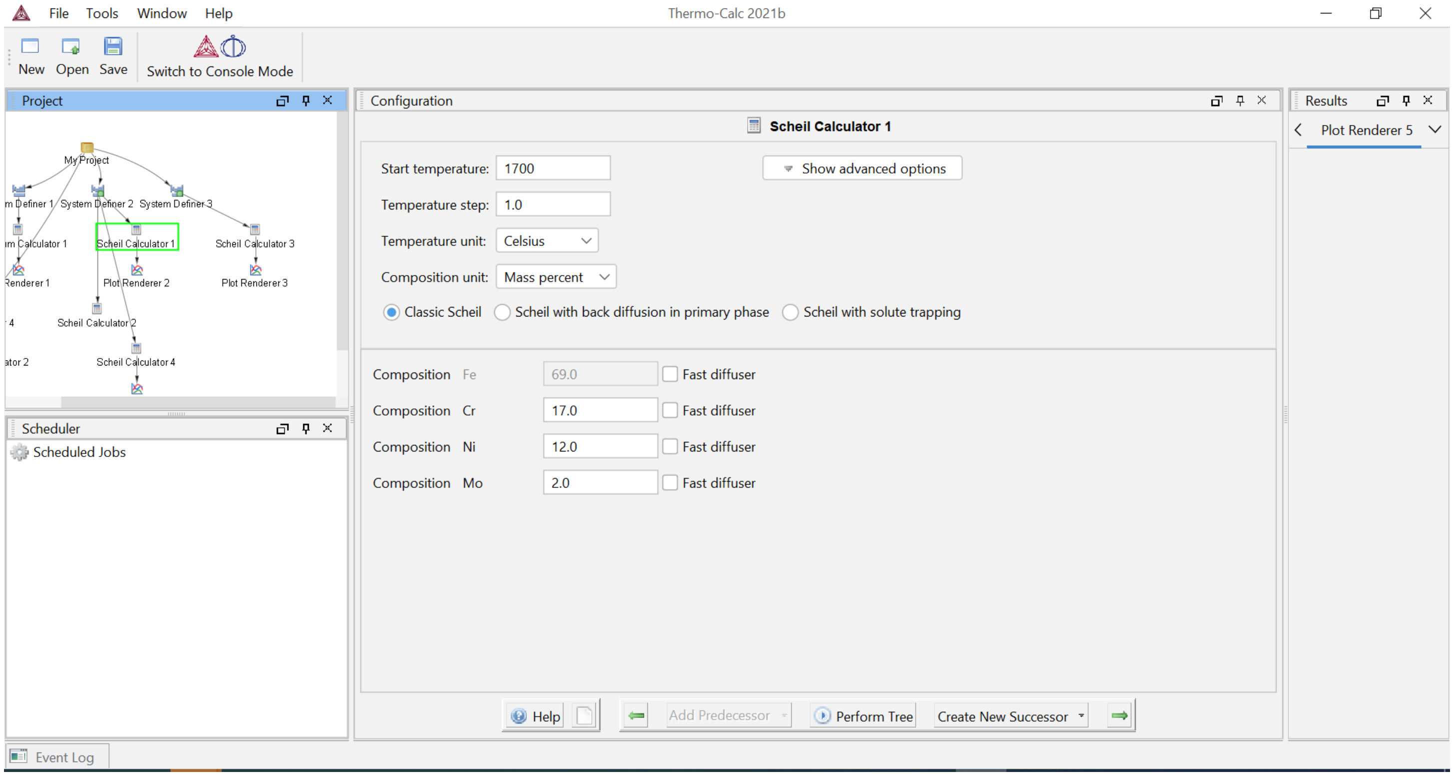




The Scheil-Gulliver module



The Scheil-Gulliver module



Scheil Calculator 1

Start temperature: 1700

Temperature step: 1.0

Temperature unit: Celsius

Composition unit: Mass percent

● Classic Scheil ○ Scheil with back diffusion in primary phase ○ Scheil with solute trapping

Composition Fe 69.0 ☐ Fast diffuser

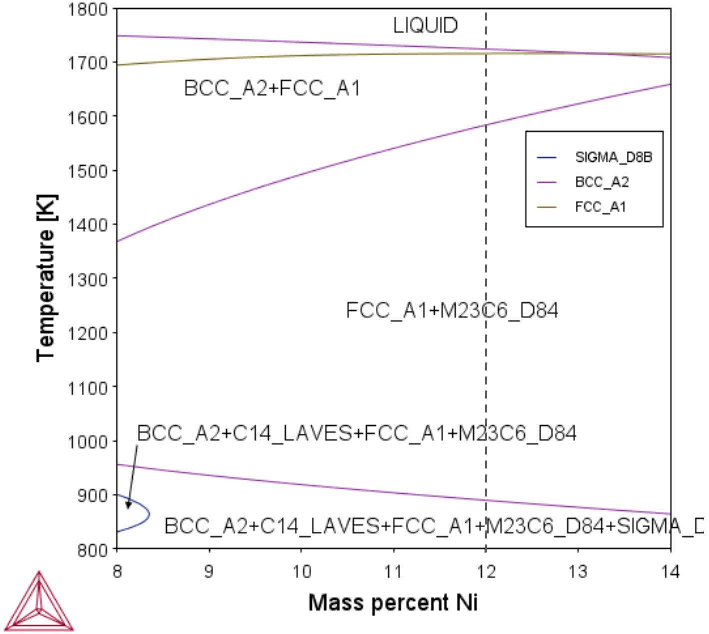
Composition Cr 17.0 ☐ Fast diffuser

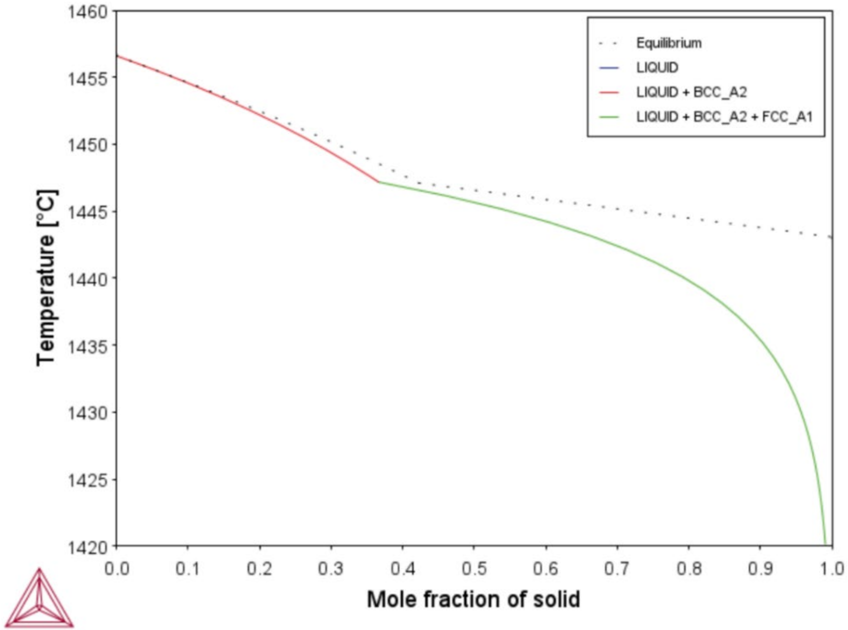
Composition Ni 12.0 ☐ Fast diffuser

Composition Mo 2.0 ☐ Fast diffuser

The Scheil-Gulliver solidification model

Solidification of 1.4404/X3CrNiMo 17-12-2





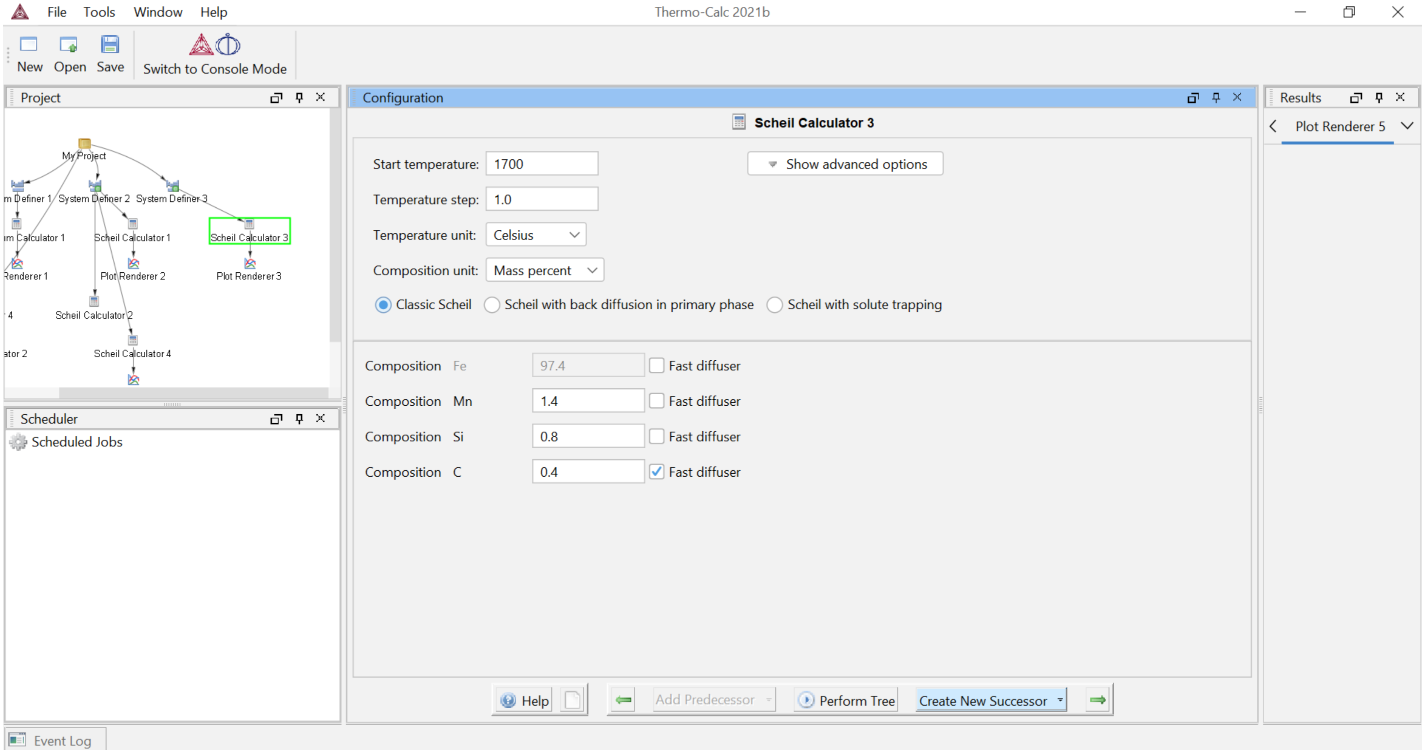
Modified Scheil-Gulliver models

S-G with fast diffusers

- Interstitial elements in steel like C, N or O have high diffusion rates
- The assumption of no diffusion in the solid phase during solidification is thus not correct at most industrial solidification rates.
- Scheil with fast diffusers is a variant of the classic Scheil simulation that was developed mainly for steel applications
- The assumptions are
  - Diffusion of all elements in the liquid phase is infinitely fast
  - Diffusion of all elements in the solid phases except the ones defined as “fast diffusers” is zero
  - Diffusion of the elements defined as “fast diffusers” is infinitely fast in the solid phase
  - The liquid/solid interface is in thermodynamic equilibrium

Modified Scheil-Gulliver models

S-G with fast diffusers



Scheil Calculator 3

Start temperature: 1700

Temperature step: 1.0

Temperature unit: Celsius

Composition unit: Mass percent

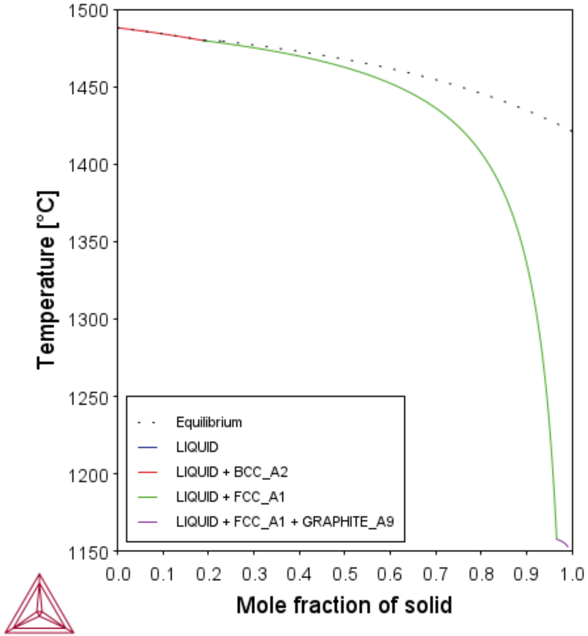
● Classic Scheil ○ Scheil with back diffusion in primary phase ○ Scheil with solute trapping

Composition	Fe	97.4	☐ Fast diffuser
Composition	Mn	1.4	☐ Fast diffuser
Composition	Si	0.8	☐ Fast diffuser
Composition	C	0.4	☑ Fast diffuser

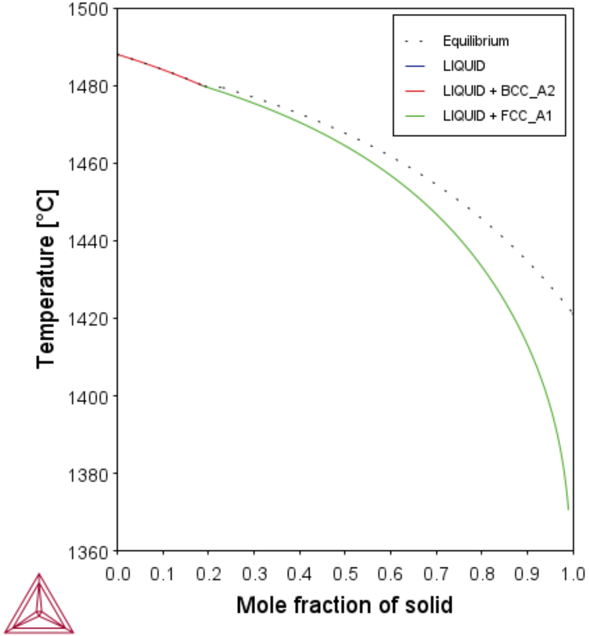
Modified Scheil-Gulliver models

Solidification of Fe-1.4Mn-0.8Si-0.4C

Classical Scheil



Modified Scheil
with C as fast diffuser



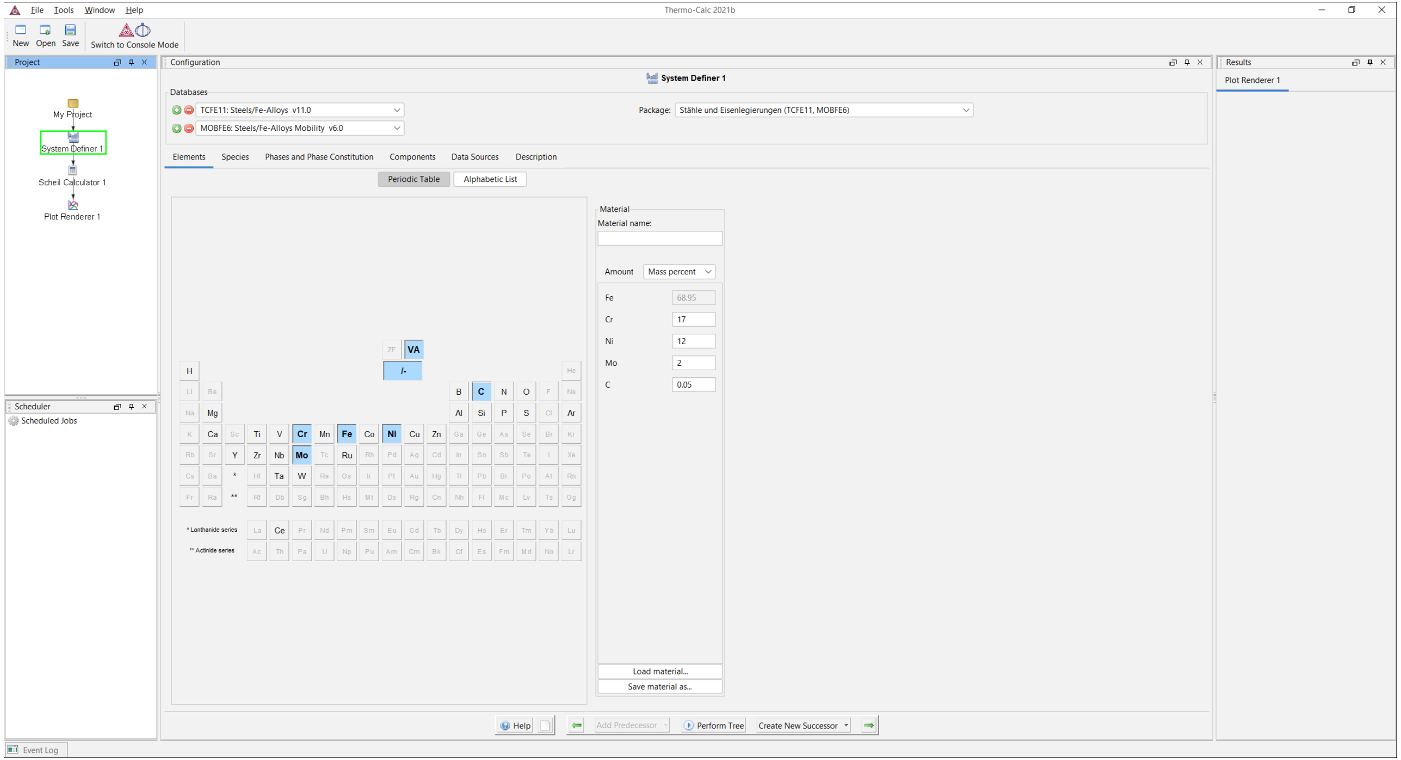
Modified Scheil-Gulliver models

S-G with back-diffusion in primary phase

- This model uses diffusion data from a mobility database to calculate back diffusion in the primary phase
- As with the Scheil-Gulliver model, this model assumes infinitely fast diffusion in the liquid material, but it allows for limited diffusion in the primary phase of the solid material.
- The assumptions are
  - Diffusion of all elements in the liquid phase is infinitely fast
  - Diffusion of all elements in the primary solid phase is quantitatively calculated using mobility data, a cooling rate, and a domain size (typically this will be the secondary arm spacing)
  - The liquid/solid interface is in thermodynamic equilibrium
- Using diffusion data from a mobility database, it quantitatively takes into account the real back diffusion of all elements in the primary solid phase (typically the FCC or BCC phase)

Modified Scheil-Gulliver models

S-G with back-diffusion in primary phase



System Definer 1

Databases:
- TCFE11: Steels/Fe-Alloys v11.0
- MOBFE6: Steels/Fe-Alloys Mobility v6.0

Package: Stähle und Eisenlegierungen (TCFE11, MOBFE6)

Material

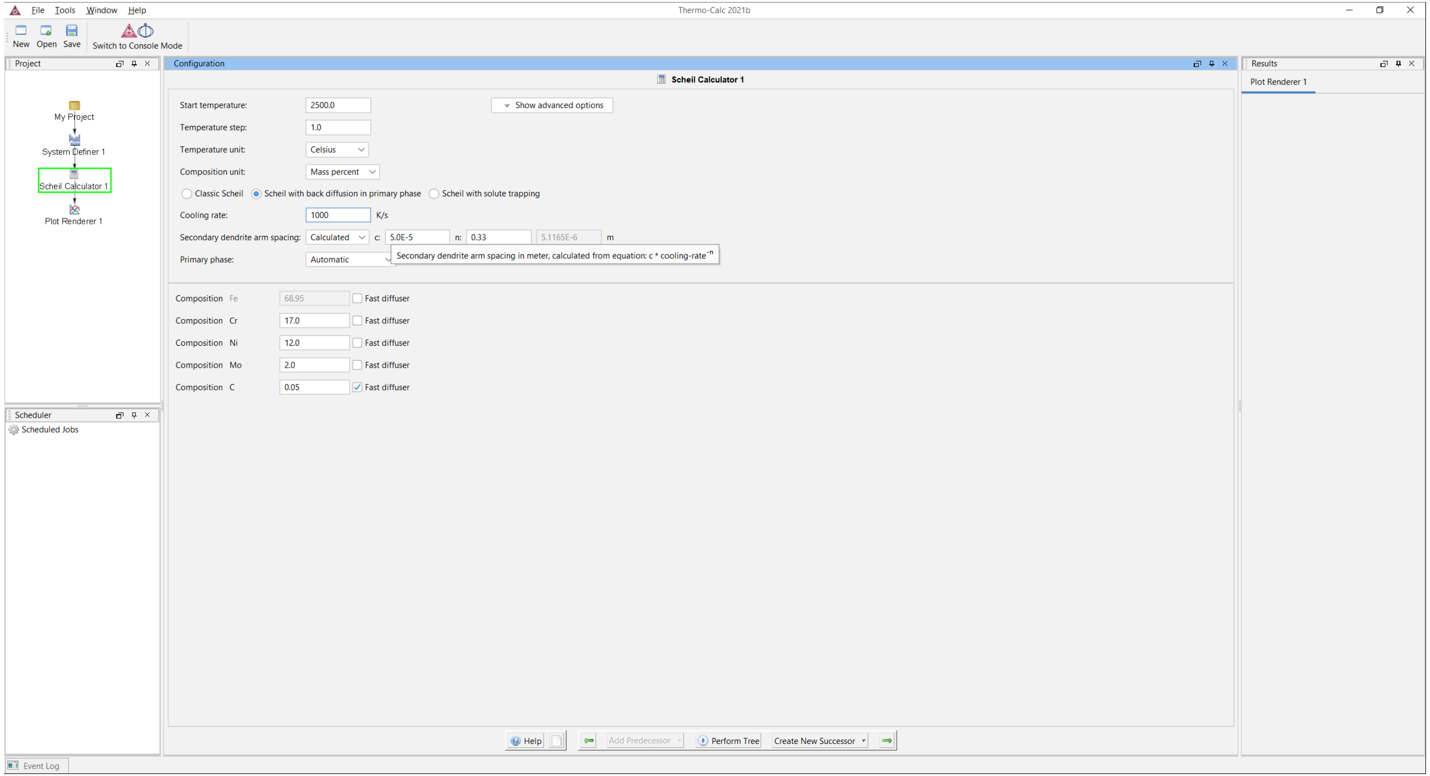
Material name:

Amount: Mass percent

Fe	68.95
Cr	17
Ni	12
Mo	2
C	0.05

Modified Scheil-Gulliver models

S-G with back-diffusion in primary phase



Scheil Calculator 1

Start temperature: 2500.0

Temperature step: 1.0

Temperature unit: Celsius

Composition unit: Mass percent

○ Classic Scheil ● Scheil with back diffusion in primary phase ○ Scheil with solute trapping

Cooling rate: 1000 K/s

Secondary dendrite arm spacing: Calculated c: 5.0E-5 n: 0.33 5.1165E-6 m

Secondary dendrite arm spacing in meter, calculated from equation: c * cooling-rate^{-n}

Primary phase: Automatic

Composition Fe 68.95 ☐ Fast diffuser

Composition Cr 17.0 ☐ Fast diffuser

Composition Ni 12.0 ☐ Fast diffuser

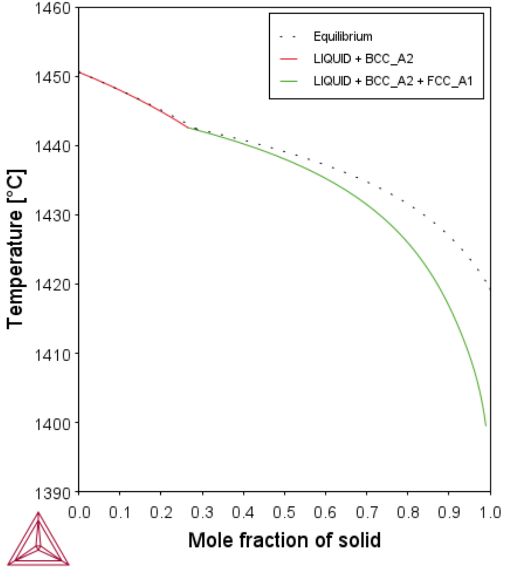
Composition Mo 2.0 ☐ Fast diffuser

Composition C 0.05 ☑ Fast diffuser

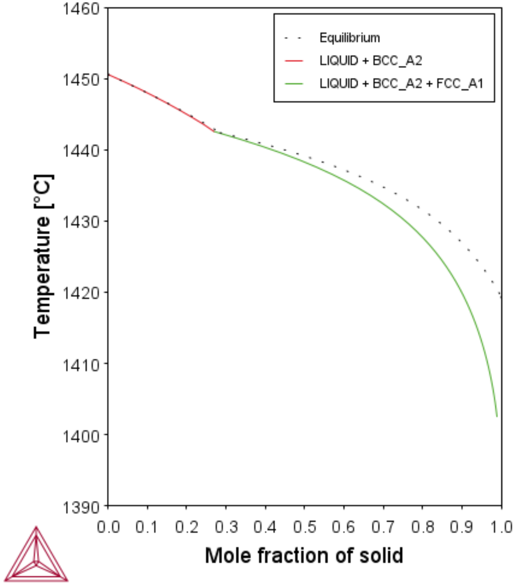
Modified Scheil-Gulliver models

Solidification of 1.4404/X3CrNiMo 17-12-2

1000 K/s



0.1 K/s



Multicomponent diffusion theory

- Fick's 1st and 2nd law describe the flux of a species k in a concentration gradient (1) and the solute balance as a function of time (2), respectively

$$J_k = -D_k \frac{\partial c_k}{\partial x} \text{ (1) and } \frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_{Bk}}{\partial x^2} \text{ (2)}$$

- If an alloy contains 2 or more species, the diffusivities D_k not only depend on the concentration but also on the concentration gradient
- A multicomponent extension to Fick's 1st law was first expressed by Onsager in 1931, postulating that each flux is linearly related to every thermodynamic force

$$J_k = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial x}$$

where the μ_i terms are the chemical potentials for the various species, which are unique functions of the composition ($\mu_i = f(c_1, c_2, c_3,\ldots,c_n)$) and L'_{ki} is the proportionality factor, which depends on the mobility of the individual species

- The flux J_k is defined such as $\sum_{k=1}^{n} V_k J_k = 0$ (V_k: partial molar volume of k)

Multicomponent diffusion theory

- Generally, it is convenient to express the fluxes as functions of gradients in concentration rather than gradients in chemical potential

$$J_k = -\sum_{i=1}^{n} L'_{ki} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial x}$$

- With $D_{kj} = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j}$ (unreduced diffusivities)

$$J_k = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial x}$$

- The $\frac{\partial \mu_i}{\partial c_j}$ values are the so-called thermodynamic factors
  → the diffusivities consist of a thermodynamic and a kinetic part

Kinetic modeling

- Atomic mobilities are purely kinetic, element specific properties, defined as the velocity of a species per unit force (unit: $\frac{m^2/s}{J/mol}$)
- The mobility coefficient for an element B in metallic matrix can be written as

$$M_B = \frac{M_B^0}{RT} \exp\left(\frac{-Q_B}{RT}\right)$$

where M_B^0 is the compositional-dependent frequency factor and Q_B the activation enthalpy

- The composition-dependency can be represented as a linear combination of the values at each endpoint of the composition space and a Redlich-Kister term

$$\Phi_B = \sum_i x_i \Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^{m} {}^{r}A_B^{i,j} \left(x_i - x_j\right)^r\right]$$

Φ_B represents lnM_B^0 or Q_B

Φ_B^i is the value of Φ_B for pure i and thus represents one of the endpoints in the composition space

${}^{r}A_B^i$ are binary interaction parameters, the commas separating different species interacting with each other

x_i and x_j are mole fractions for elements i and j, respectively

- As in the case of thermodynamic data, the model parameters $\Phi_B^i, {}^{r}A_B^i$,… are determined by an optimization procedure (considering experimental data)

Kinetic modeling

- The multi-component diffusion theory has been implemented in DICTRA (now TC diffusion module)
- The mobilities are stored in the mobility databases
- The reason to store individual mobilities rather than interdiffusion coefficients is that in an n-component system, there are n mobilities and $(n-1)^2$ interdiffusion coefficients
- The mobilities are related to the interdiffusion coefficients according to

$$L'_{ki} = \sum_{i=1}^{n} (\delta_{ik} - c_k V_i)\, c_i y_{va} M_i$$

δ_{ik} is the Kronecker delta, i.e. $\delta_{ik} = 1$ when j=k and $\delta_{ik} = 0$ otherwise

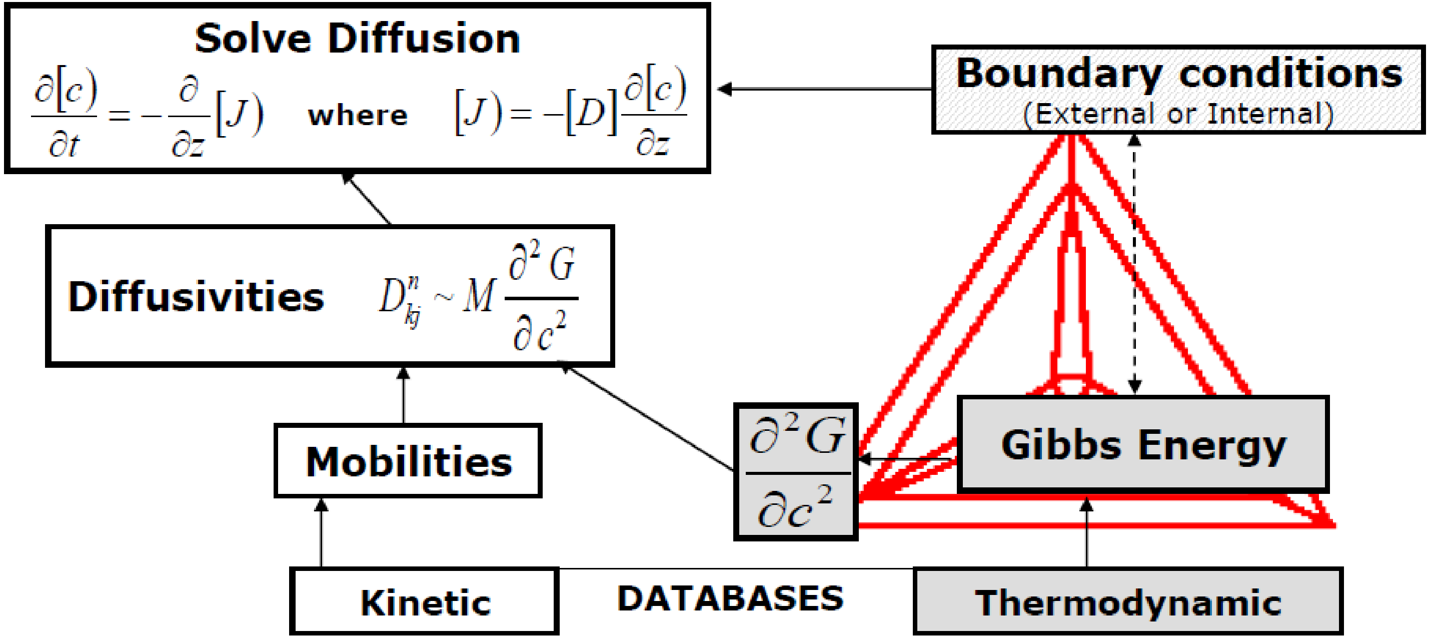
c_k and c_i are the amounts of k and i per unit volume

V_i is the partial molar volume of element i

y_{va} is the fraction of vacant lattice sites on the sublattice where i is dissolved

M_i is the mobility of i when i is interstitial and the mobility divided by y_{va} when i is substitutionally dissolved

Kinetic modeling withe Thermo-Calc



Solve Diffusion

$$\frac{\partial[c)}{\partial t} = -\frac{\partial}{\partial z}[J) \quad \text{where} \quad [J) = -[D]\frac{\partial[c)}{\partial z}$$

Boundary conditions

(External or Internal)

Diffusivities $D_{kj}^{n} \sim M \frac{\partial^2 G}{\partial c^2}$

Mobilities

$\frac{\partial^2 G}{\partial c^2}$

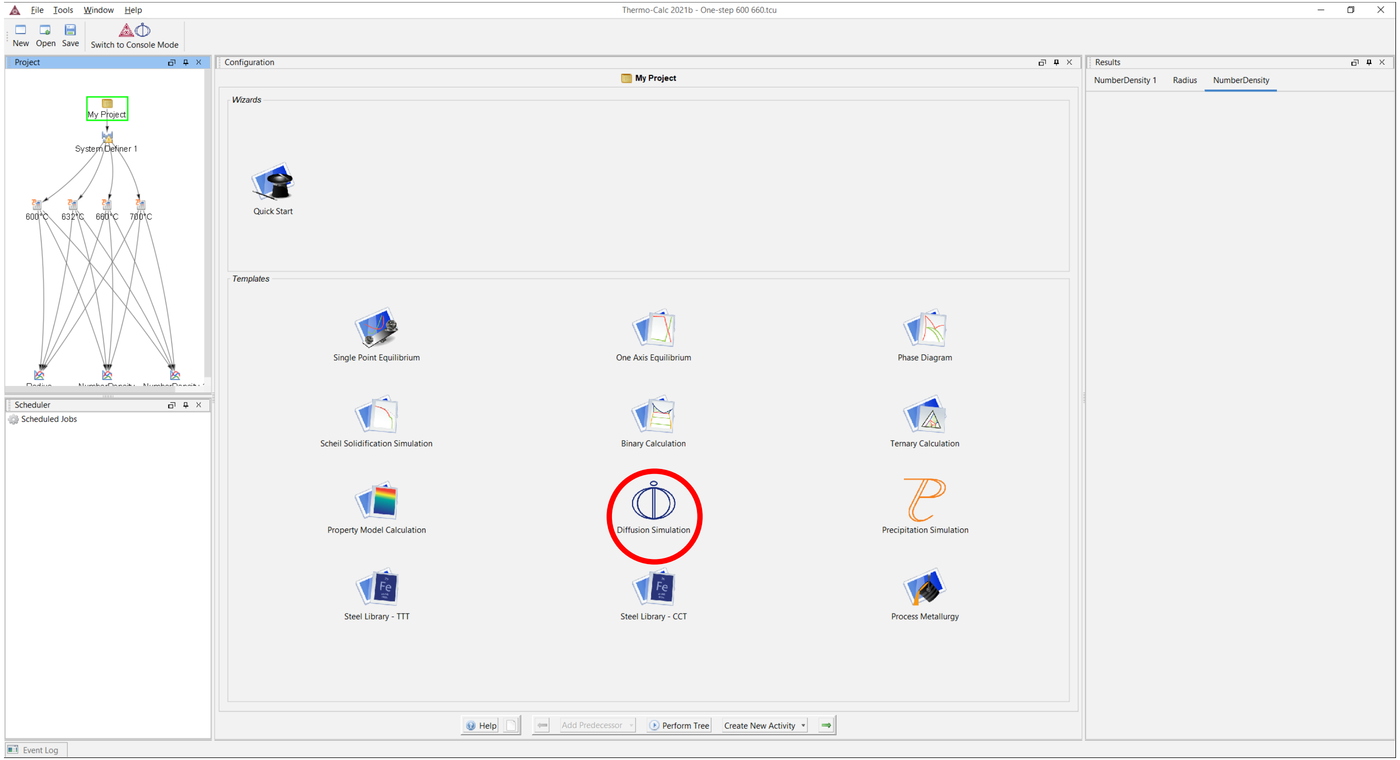
Gibbs Energy

Kinetic

DATABASES

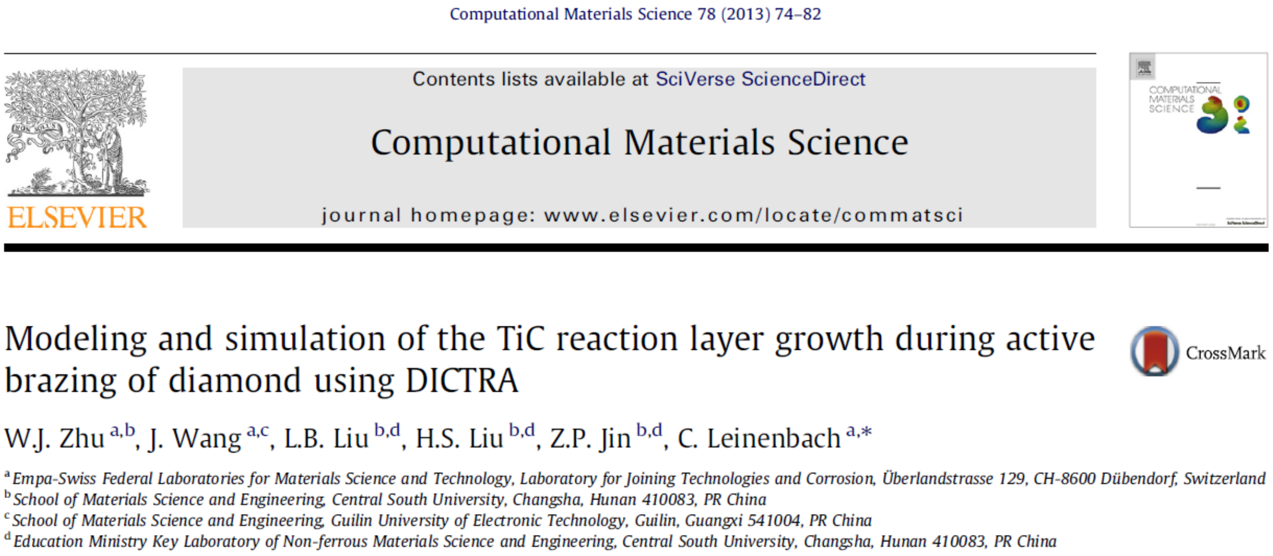
Thermodynamic

The diffusion simulation module



The diffusion simulation module

Example: Brazing of diamond (C) to steel



Computational Materials Science 78 (2013) 74–82

Contents lists available at SciVerse ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

ELSEVIER

Modeling and simulation of the TiC reaction layer growth during active brazing of diamond using DICTRA

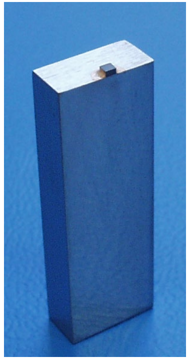
W.J. Zhu [a,b], J. Wang [a,c], L.B. Liu [b,d], H.S. Liu [b,d], Z.P. Jin [b,d], C. Leinenbach [a,*]

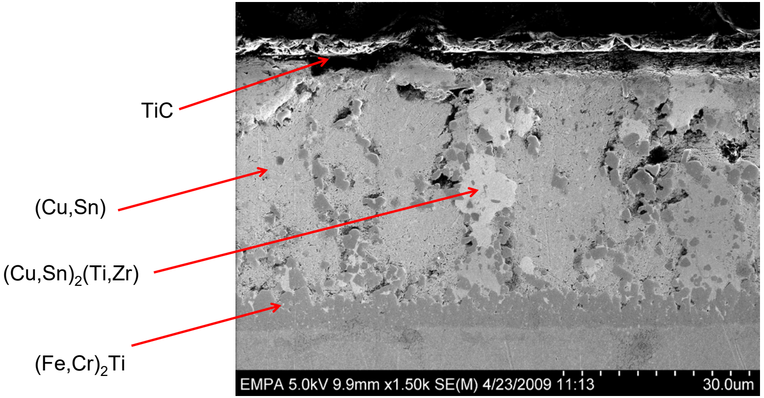
[a] *Empa-Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Joining Technologies and Corrosion, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*
[b] *School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China*
[c] *School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin, Guangxi 541004, PR China*
[d] *Education Ministry Key Laboratory of Non-ferrous Materials Science and Engineering, Central South University, Changsha, Hunan 410083, PR China*

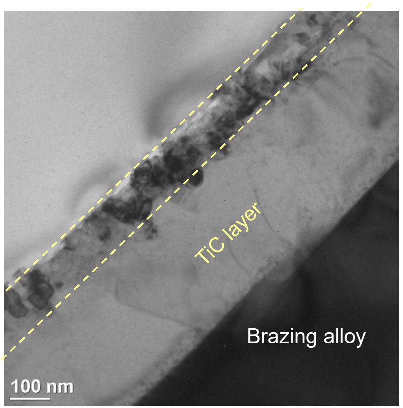
The diffusion simulation module

Example: Brazing of diamond (C) to steel

- Vacuum brazing 930 ºC /10 min
- Filler: Cu-14.4Sn-10.2Ti-1.5Zr (mass %)
- Base material: X2Cr Ni Mo 18 14 3 stainless steel (AISI 316)
- Thickness of brazing layer: ~50 µm







The diffusion simulation module

Example: Brazing of diamond (C) to steel

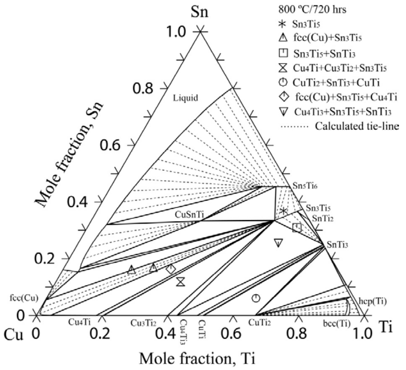
Thermodynamics

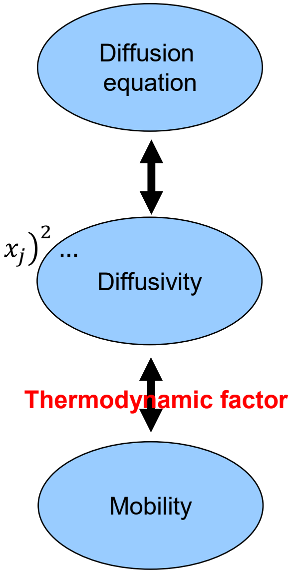
$$G_{mix} = G^0 + G^{ideal}_{mix} + G^{excess}_{mix}$$

$$G_{mix} = \sum_i x_i G_i^0 + RT\sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij}$$

$$\Omega^{\phi}_{i,j} = {}^{0}\Omega^{\phi}_{i,j} + {}^{1}\Omega^{\phi}_{i,j}(x_i - x_j) + ({}^{1}\Omega^{\phi}_{i,j})^2(x_i - x_j)^2 \ldots$$

$${}^{k}\Omega^{\phi}_{i,j} = A + BT + CT\ln T$$





Kinetics/Diffusion

$$J_k = -\sum_{i=1}^{n} D^n_{kj} \nabla \cdot c_i \qquad \frac{\partial c_k}{\partial t} = -\nabla \cdot J_k$$

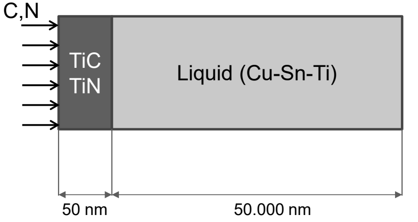
$$D^n_{kj} = \sum_{i=1}^{n} (\delta_{ik} - x_k) x_i M_i \left(\frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_i}{\partial x_n}\right)$$

$$M_B = \exp\left(\frac{-Q_B + RTLnM_B^0}{RT}\right)\frac{1}{RT}{}^{mg}\Omega$$

$$= \exp\left(\frac{\Delta G^*}{RT}\right)\frac{1}{RT}{}^{mg}\Omega$$

$$\Delta G^* = \Phi_B$$

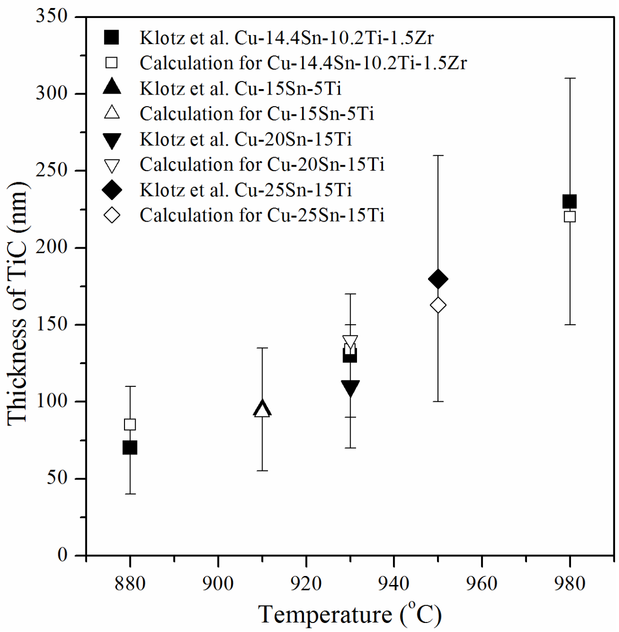
$$= \sum_i x_i \Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^{m} {}^{r}\Phi_B^{i,j}(x_i - x_j)^r\right]$$



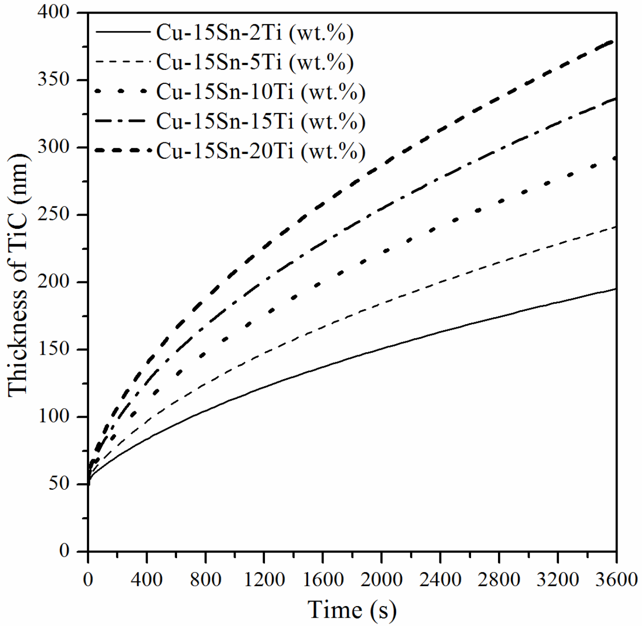
The diffusion simulation module

Example: Brazing of diamond (C) to steel

- Simulated influence of alloy composition + experimental results



- Simulated influence of amount of Ti on TiC growth in brazing diamond at 930°C

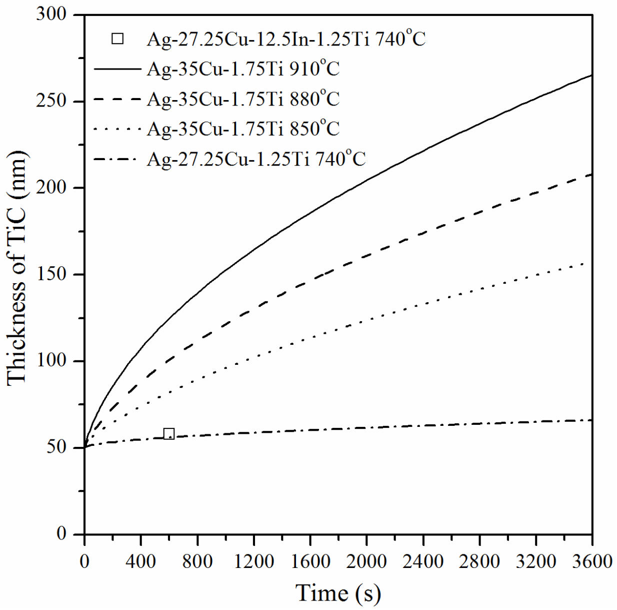


/W.J. Zhu, C. Leinenbach et al, Comp. Mater. Sci. 78 (2013) 74./

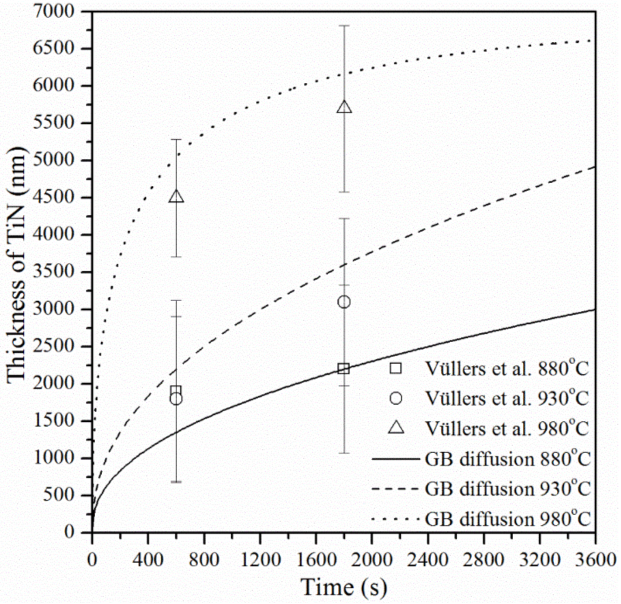
The diffusion simulation module

Example: Brazing of diamond (C) to steel

- Simulated influence of Ag-based filler alloy



- TiN reaction layer growth during brazing of AlN ceramics

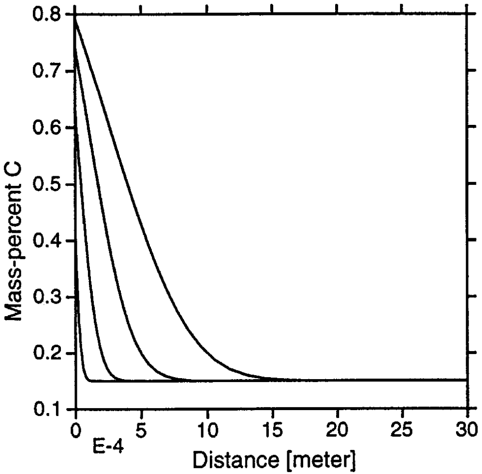


/W.J. Zhu, C. Leinenbach et al, Comp. Mater. Sci. 78 (2013) 74./

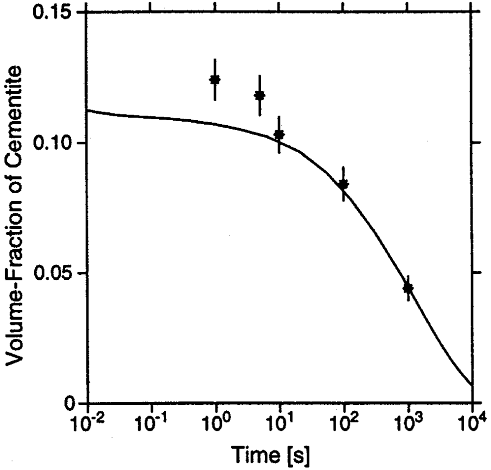
The diffusion simulation module

Other examples

Calculated C-concentration profiles after 100, 1000, 5’000 and 18’000 s at 900°C in a carburizing atmosphere



Calculated volume fraction of cementite as a function of time, during austenitization of an Fe-2.06 at.% Cr-3.91 at.% C alloy at 910°C



/A. Borgenstam et al., Journal of Phase Equilibria 21(3) (2000)

Simulation of precipitation reactions

- Phase transformations start with the formation of stable nuclei of a size larger than the critical radius grown at expenses of available elements in the matrix.
- The growth of the nucleus ends when the thermodynamic equilibrium is reached, i.e. chemical potentials of each element are equal anywhere in the system.
- Assuming spherical nuclei, the nucleation rate can be described as

$$J(t) = J_s exp\left(-\frac{\tau}{t}\right)$$

J_s: steady state nucleation rate
τ: incubation time

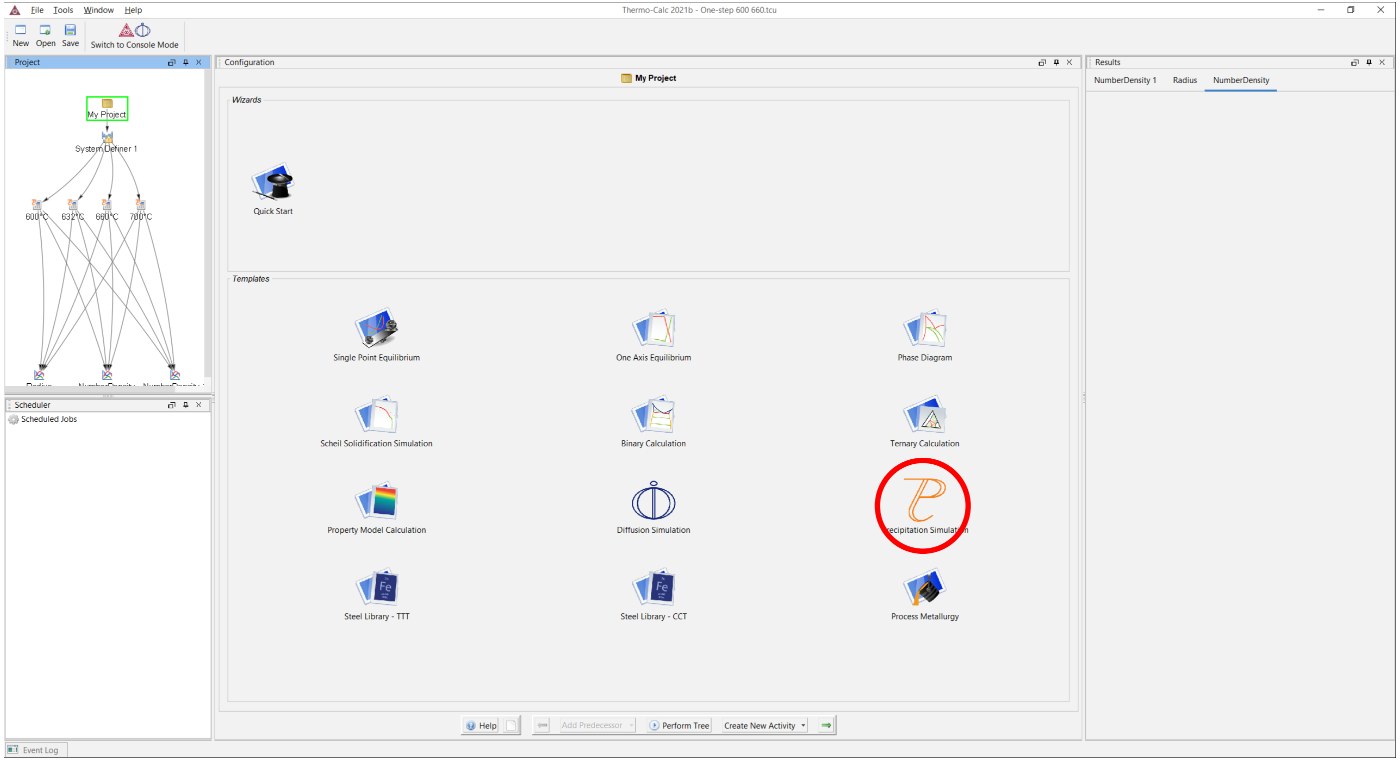
$$J_s = Z\beta^* N_0 exp\left(-\frac{\Delta G^*}{kT}\right)$$

Z: Zeldovich factor
β^*: rate at which atoms are attached to critical nucleus
N_0: number of available nucleation sites per unit volume
ΔG^*: nucleation barrier

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_V^{\alpha\to P}}$$

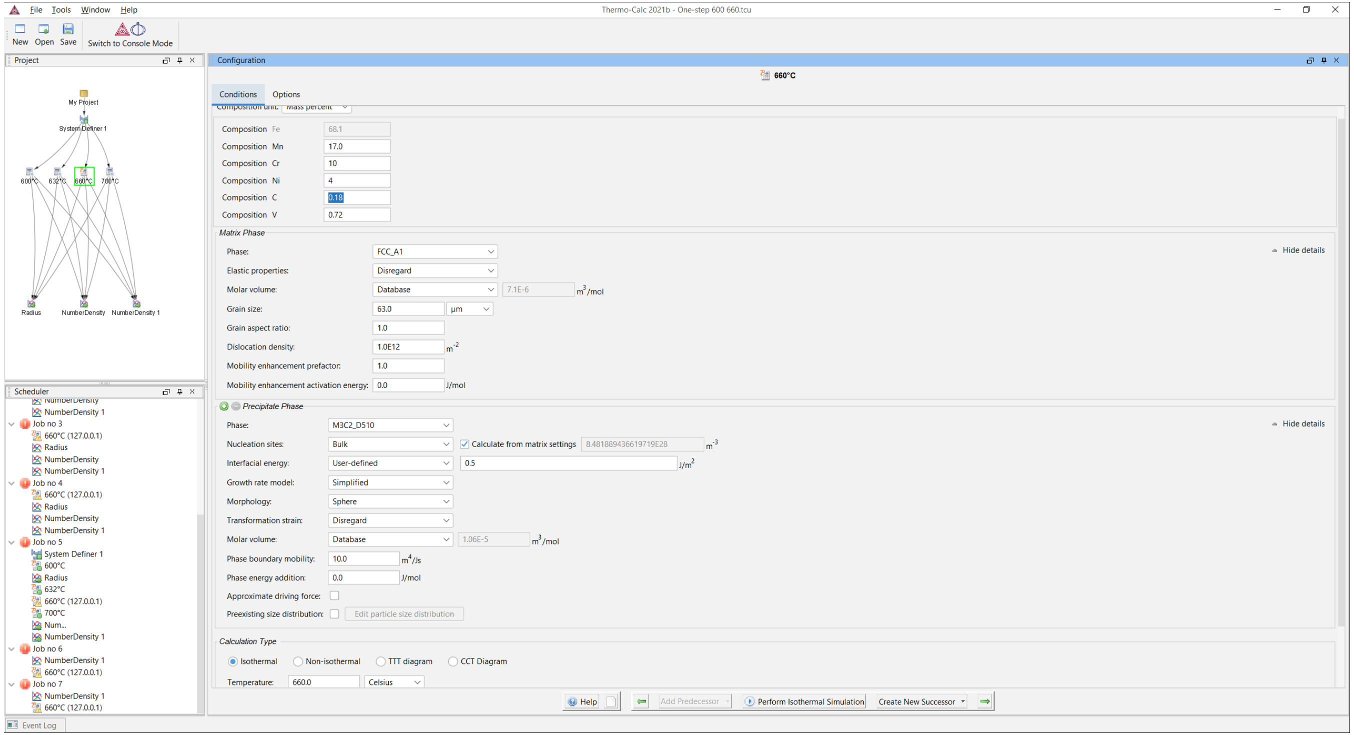
σ: interfacial energy
$\Delta G_V^{\alpha\to P}$: driving force for formation of precipitates P from α matrix

The precipitation module



The precipitation module

Example: Carbide precipitation in Fe shape memory alloy



Composition unit: Mass percent

Composition Fe: 68.1
Composition Mn: 17.0
Composition Cr: 10
Composition Ni: 4
Composition C: 0.18
Composition V: 0.72

Matrix Phase

Phase: FCC_A1
Elastic properties: Disregard
Molar volume: Database 7.1E-6 m^3/mol
Grain size: 63.0 µm
Grain aspect ratio: 1.0
Dislocation density: 1.0E12 m^{-2}
Mobility enhancement prefactor: 1.0
Mobility enhancement activation energy: 0.0 J/mol

Precipitate Phase

Phase: M3C2_D510
Nucleation sites: Bulk ☑ Calculate from matrix settings 8.481889436619719E28 m^{-3}
Interfacial energy: User-defined 0.5 J/m^2
Growth rate model: Simplified
Morphology: Sphere
Transformation strain: Disregard
Molar volume: Database 1.06E-5 m^3/mol
Phase boundary mobility: 10.0 m^4/Js
Phase energy addition: 0.0 J/mol
Approximate driving force: ☐
Preexisting size distribution: ☐ Edit particle size distribution

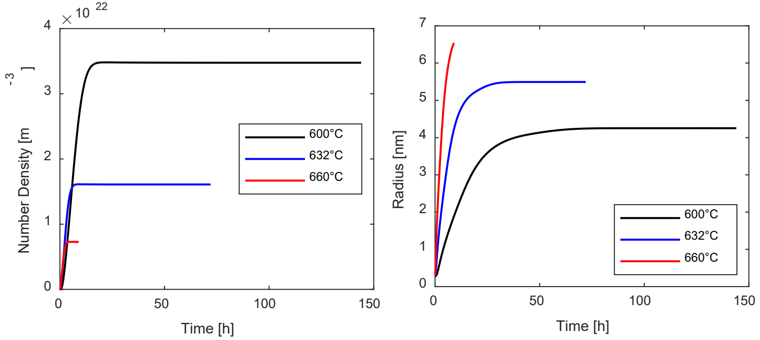
Calculation Type

● Isothermal ○ Non-isothermal ○ TTT diagram ○ CCT Diagram

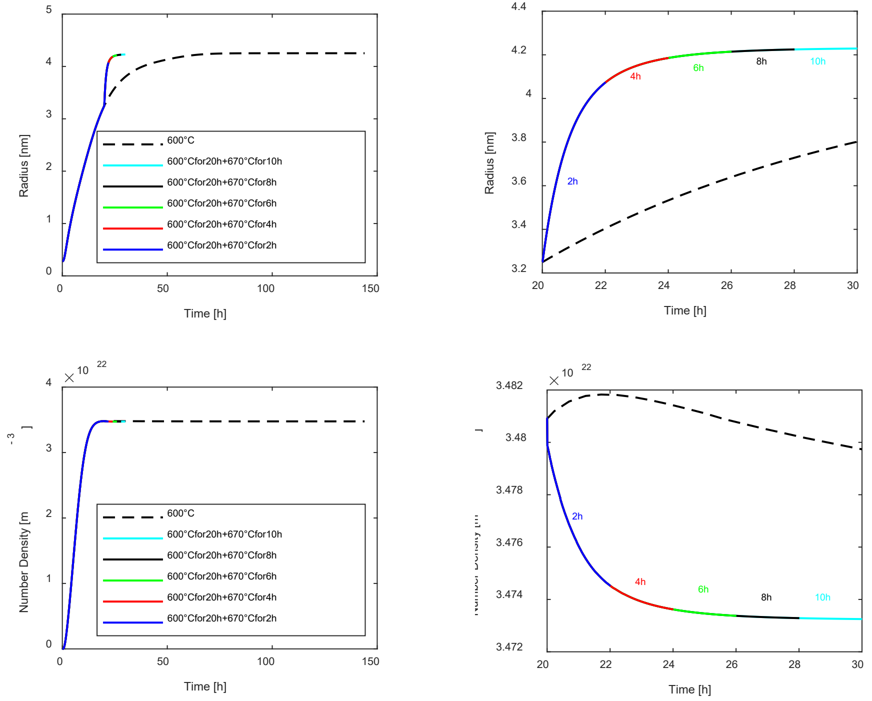
Temperature: 660.0 Celsius

The precipitation module

Example: Carbide precipitation in Fe shape memory alloy



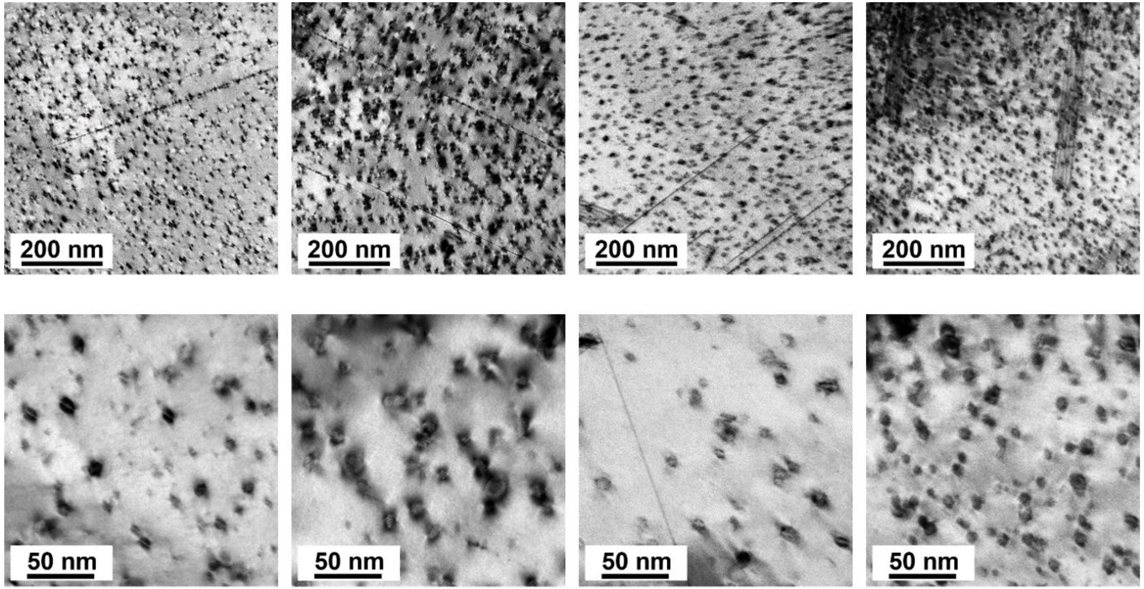
Conditions		TEM	0.68	0.69	0.7	0.71
600 °C for 144 h	Radius [nm]	3.3	3.2	3.7	4.3	4.9
	Number density $[1/m^3]$	1.5E22	8.1E22	5.3E22	3.5E22	2.2E22
660 °C for 9 h	Radius [nm]	4.5	5.1	5.8	6.5	7.2
	Number density $[1/m^3]$	6.7E21	1.9E22	1.2E22	7.3E21	4.4E21



- Yajiao, Y. A. N. G., Christian Leinenbach, and Moslem Shahverdi. "Simulation and experimental characterization of VC precipitation and recovery stress formation in an FeMnSi-based shape memory alloy." Journal of Alloys and Compounds (2023): 168856.

The precipitation module

Example: Carbide precipitation in Fe shape memory alloy


600 °C (20 h) + 670 °C (2 h) + 670 °C (6 h)

600 °C (20 h) + 670 °C (6 h)

600 °C (41 h) + 670 °C (6 h)

600 °C (4 h)

Condition	TEM		Simulation	
	Radius [nm]	NrDensity [1/m³]	Radius [nm]	NrDensity [1/m³]
600 °C (20 h) + 670 °C (2 h)	2.9	1.4E+22	4.1	3.5E+22
600 °C (20 h) + 670 °C (6 h)	3.8	1.1E+22	4.2	3.5E+22
600 °C (4 h) + 670 °C (6 h)	5.2	7.0E+21	6.0	1.1E+22
600 °C (20 h) + 670 °C (6 h)	3.8	1.1E+22	4.2	3.5E+22
600 °C (41 h) + 670 °C (6 h)	3.9	1.6E+22	4.2	3.5E+22
600 °C for 144 h	3.3	1.5E+22	4.3	3.5E+22
600 °C (20 h) + 670 °C (6 h)	3.8	1.1E+22	4.2	3.5E+22
600 °C (41 h) + 670 °C (6 h)	3.9	1.6E+22	4.2	3.5E+22