MATGEN-IV
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Equilibrium Phase Diagrams

- Training course -

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Contents

1. Basic Thermodynamics

1.1. Definition and experimental determination of an equilibrium phase diagram
1.2. Thermodynamic study of phase diagrams and minimisation of the Gibbs free energy
From the Gibbs free energy variations of the phases, G(X,T),
to the determination of the phase diagram (X: Composition, T: Temperature)

2. Introduction to “CALPHAD” formalism

CALPHAD = CALculation of PHase Diagrams

From experimental data to G(X,T) thermodynamic polynomial functions

2.1. Thermodynamical models for solutions and compounds → G(X,T)
2.2. Refinements of the model parameters based on selected experimental datasets

3. Introduction to the Thermo-Calc software. Demonstrations and examples

3.1. Thermo-Calc software = CALPHAD formalism + Thermodynamic databases of G(X,T)
Calculation of phase equilibria by Gibbs energy minimisation process
3.2. Demonstrations and working examples: Two cases (Cu-Ni and Fe-Cr systems)

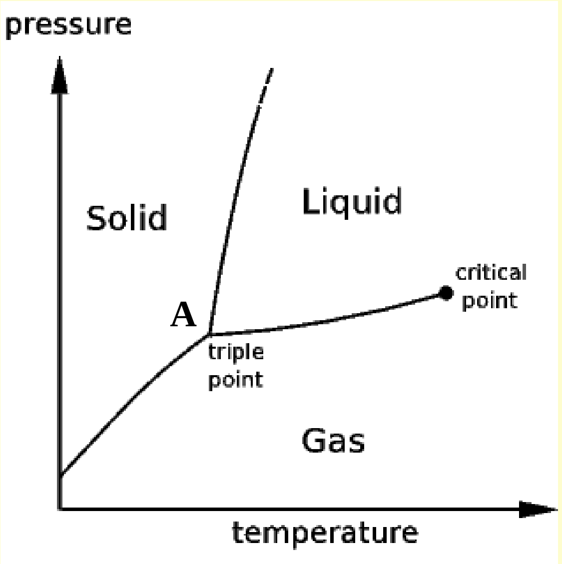
What is an equilibrium phase diagram?

- Graphical representation of the **lines of equilibrium** or **phase boundaries**: lines that demarcate where phase transitions occur

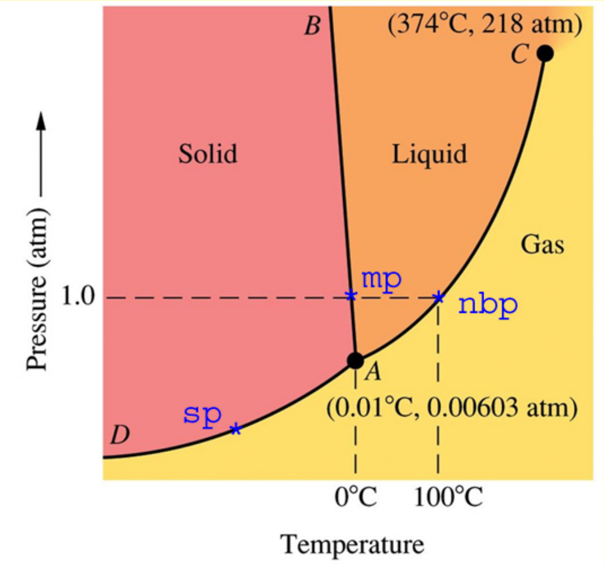
☞ Single (pure) substance: Pressure-temperature diagram

Triple point: the unique intersection of the lines of equilibrium between three states of matter, usually solid, liquid, and gas

Pressure-Temperature diagram: general case



phase diagram of **water**



A: Triple point

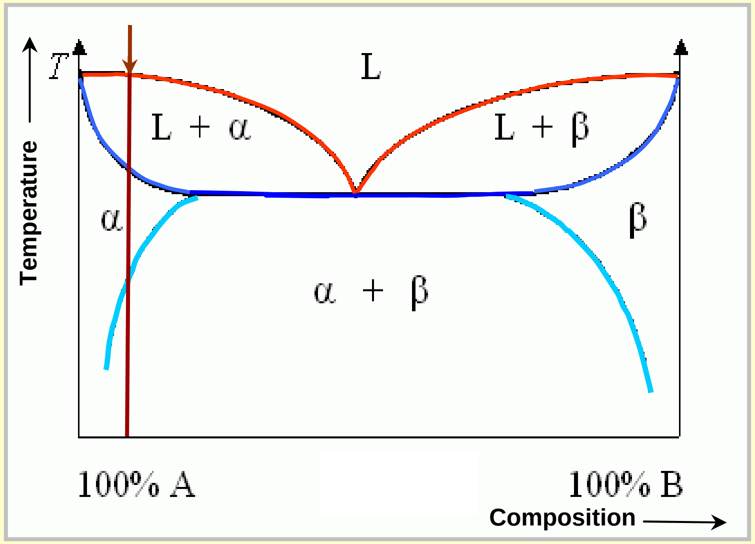
sp, **mp**, **nbp**: sublimation, melting, normal boiling points

1.1. Definition and experimental determination of an equilibrium phase diagram

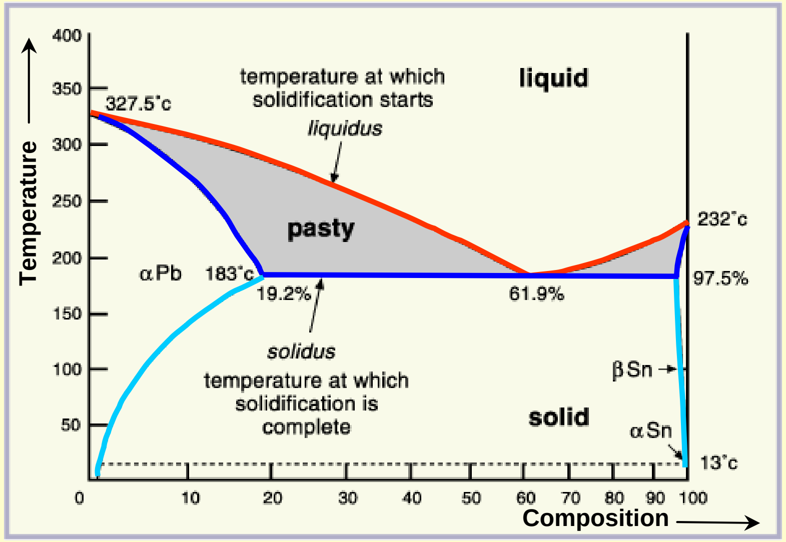
☞ Two-component or Binary phase diagrams: Temperature-composition diagram, P constant

- **Liquidus**: the line above which the alloy is properly in a **liquid** (L) state
- **Solidus**: the line below which the alloy is properly in a **solid** (α) state
- **Solvus**: the line which represents the **limit of solid solubility** of a phase

Temperature-composition diagram



Binary phase diagram of **Pb-Sn**



Composition (concentration): **Mole** or **mass fraction** (**or percent**) of a constituent i in a given alloy

X_A and X_B **mole fractions** of A and B: $\boxed{X_A = n_A / N}$ $\boxed{X_B = n_B / N}$ $\boxed{X_A + X_B = 1}$

w_A and w_B **mass fractions** of A and B:
C_A and C_B **mass percents**

$\boxed{w_A = m_A / M}$ $\boxed{w_B = m_B / M}$ $\boxed{w_A + w_B = 1}$

- n_A and n_B : number of moles of A and B; m_A and m_B mass of A and B;
- $N = n_A + n_B$: total mole number ; $M = m_A + m_B$: total mass;

Experimental determination of a phase diagram

Thermal analysis techniques

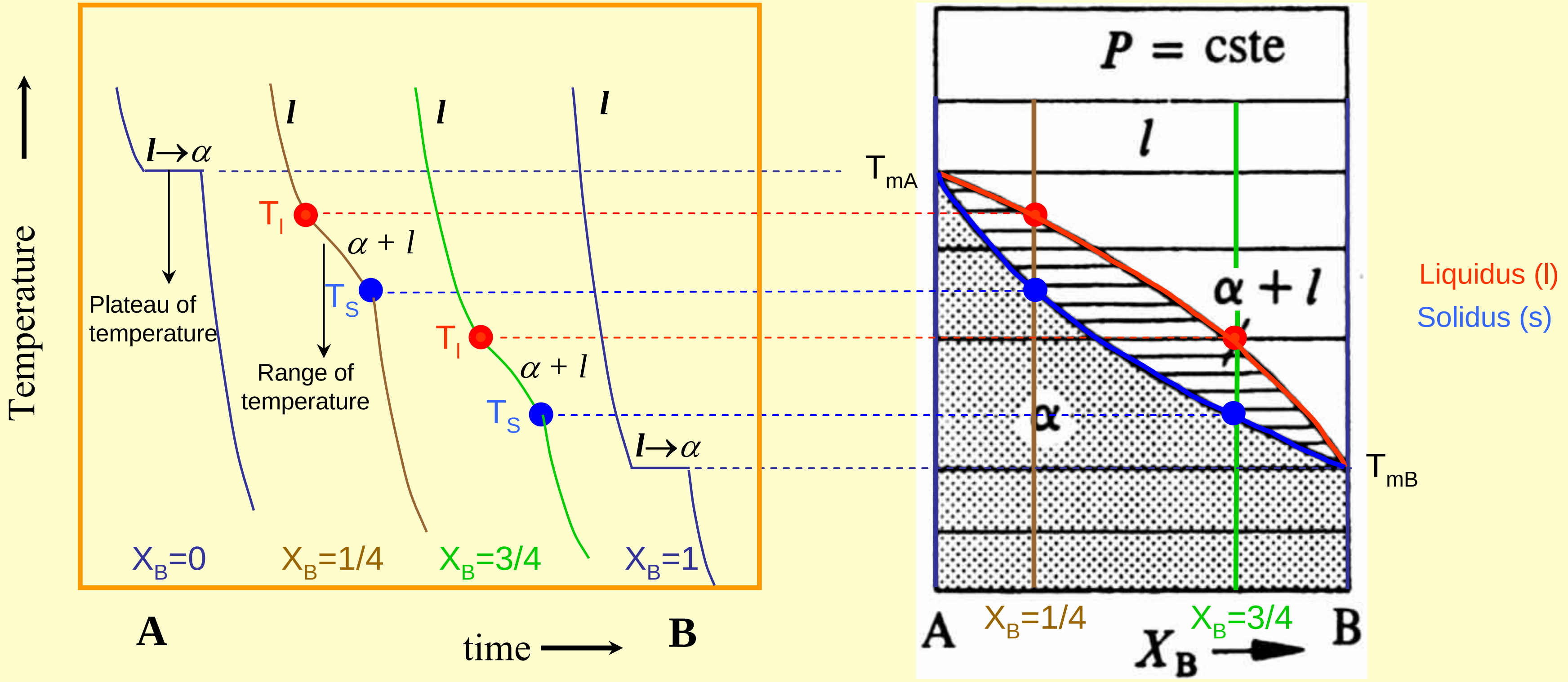
- T = f (t) cooling curves measurements for several compositions

☞ **Pure** compound: Fusion/Solidification or allotropic transition ↔ solidification at 1 transition temperature

☞ **Binary** solution: Fusion/Solidification ↔ solidification in a range of temperature

↳ liquidus and solidus

Temperature = f(time) ⇨ Temperature = f(composition)



- More advanced techniques: DSC / DTA (Differential Scanning calorimetry / Thermal Analysis)

Gibbs free energy

❶ First law of thermodynamics: conservation of the energy in any process
Introduction of the **internal energy** E
Introduction of the **enthalpy** function $H = E + PV$ and $dH = dE + PdV + VdP$

❷ Second law of thermodynamics
Introduction of the **entropy** function S and $dS = dQ/T$

❸ Third law of thermodynamics
Introduction of the **Gibbs free energy** function: $G = H - TS = E + PV - TS$
And $dG = dH - SdT - TdS = dE + PdV + VdP - SdT - TdS$

☞ **Closed** system: $dE = dW + dQ = -PdV + TdS$ $\boxed{dG = VdP - SdT}$

☞ **Open** system: $dE = dW + dQ + \Sigma\mu_i dn_i = -PdV + TdS + \Sigma\mu_i dn_i$ $\boxed{dG = VdP - SdT + \Sigma\mu_i dn_i}$

chemical energy contribution

$$\mu_i = \bar{G}_i = \left(\frac{dG}{dn_i}\right)_{T,P,nj}$$

chemical potential of component i, or
partial molar Gibbs free energy

Molar Gibbs energy and chemical potentials

- The Gibbs free energy G of a system is the sum of the chemical potentials of its constituents

T,P constant $$\boxed{G = \Sigma n_i \mu_i}$$

- The molar Gibbs free energy G_m = Gibbs free energy of one mole of the substance

T,P constant $$\boxed{G_m = \Sigma x_i \overline{G}_i = \Sigma x_i \mu_i}$$

X_i molar fraction of component i

➪ **One-component (A) system:** $X_A=1$

$$\boxed{G_m = \overline{G}_A = \mu_A}$$

The chemical potential of this component is identical to its molar Gibbs free energy

➪ **Binary system (A and B):** X_A and X_B varying with $X_A+X_B=1$

$$\boxed{G_m = x_A \overline{G}_A + x_B \overline{G}_B = x_A \mu_A + x_B \mu_B}$$

Equilibrium criteria (1/2)

- Spontaneous transformation ↔ decrease of Gibbs free energy of the system
- Equilibrium condition: **dG = 0** ↔ Gibbs free energy of the system is minimum

☞ Closed system. One-component (A) system

If a substance A may be either in the α or β structure (phase) associated to G^α and G^β

The stable structure is that which corresponds to the lowest Gibbs free energy of the system

- α more stable than β ↔ $\boxed{G_A^\alpha < G_A^\beta}$
- At equilibrium ↔ $\boxed{G_A^\alpha = G_A^\beta}$ α and β coexist

Equilibrium criteria (2/2)

☞ Open system. Two component or Binary system (1 and 2) or (A and B)

Considering: two phases α and β at equilibrium respectively associated to G^α and G^β

➥ total free energy change of the system: $dG = dG^\alpha + dG^\beta$

$$\text{T,P constant} \quad \begin{cases} dG^\alpha = \mu_1^\alpha\, dn_1^\alpha + \mu_2^\alpha\, dn_2^\alpha \\ dG^\beta = \mu_1^\beta\, dn_1^\beta + \mu_2^\beta\, dn_2^\beta \end{cases}$$

As the total amount of 1 and 2 are constant → $dn_1^\alpha = - dn_1^\beta$ and $dn_2^\alpha = - dn_2^\beta$

$$dG = \mu_1^\alpha\, dn_1^\alpha + \mu_2^\alpha\, dn_2^\alpha - \mu_1^\beta\, dn_1^\alpha - \mu_2^\beta\, dn_2^\alpha$$

$$dG = (\mu_1^\alpha - \mu_1^\beta)\, dn_1^\alpha + (\mu_2^\alpha - \mu_2^\beta)\, dn_2^\alpha$$

As dn_1^α and dn_2^α are independent,

at equilibrium, **dG = 0** $\Rightarrow$ $\boxed{\mu_1^\alpha = \mu_1^\beta \;\text{ and }\; \mu_2^\alpha = \mu_2^\beta}$

for each component, equality of the chemical potentials in all phases (no chemical transfer)

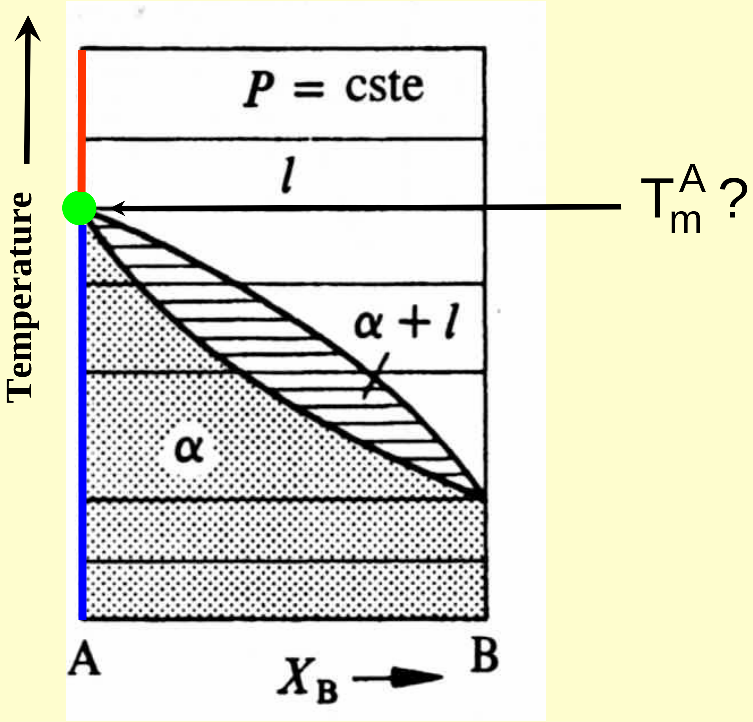
- **Pure compounds**: melting points (T_m) determinations

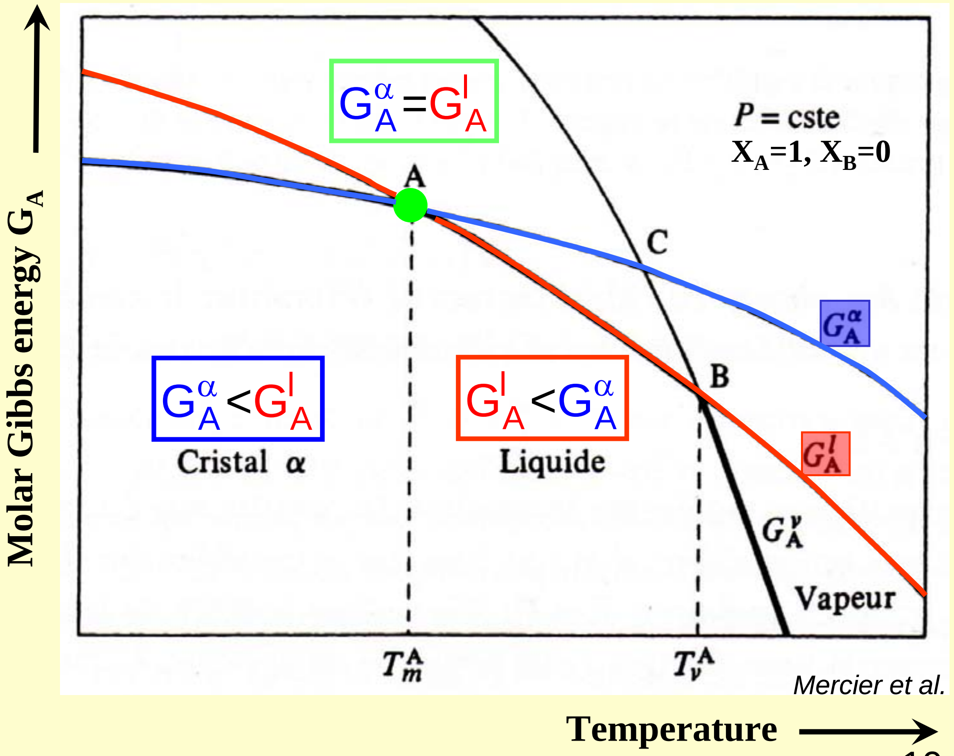
Considering pure compound A (X_B=0): How to determine its melting temperature T_m^A ?

α: solid phase ⟷ $G_A^\alpha(T)$

l: liquid phase ⟷ $G_A^l(T)$

$$\boxed{T_m^A \leftrightarrow G_A^\alpha = G_A^l}$$





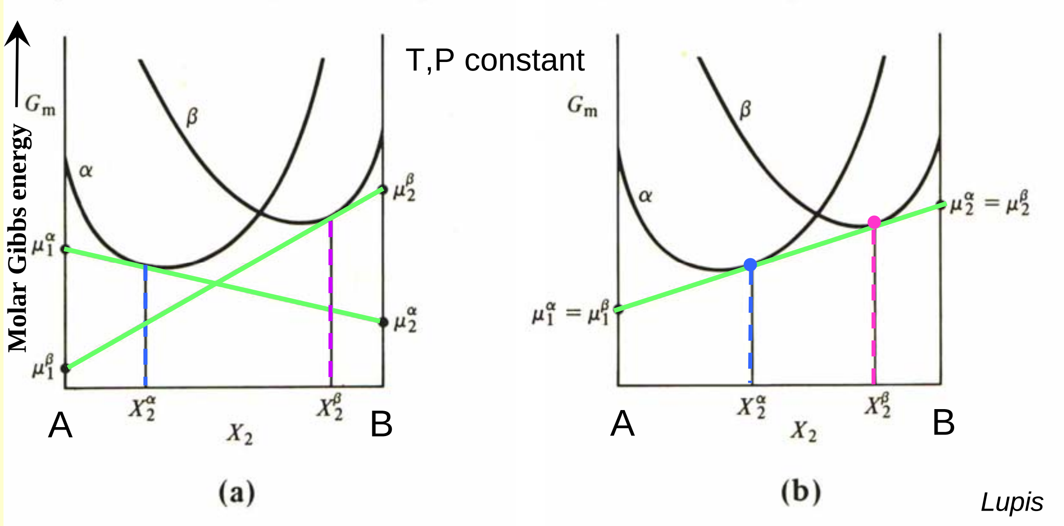
Mercier et al.

- **Binary systems**: determinations of the liquidus, solidus and solvus

Chemical potentials and common tangent construction (1/4)

• Equilibrium phases and equilibrium compositions

➢ Graphical representations of the chemical potentials of the two components by the method of intercepts:



Lupis

(a) α and β not in equilibrium (b) α and β in equilibrium

The intercepts of the two axes by the tangent of the Gibbs free energy curve of the α phase at the composition X_2^α represent μ_1^α and μ_2^α

Idem for the β phase

➢ Equilibrium condition:

$$\mu_1^\alpha = \mu_1^\beta \text{ and } \mu_2^\alpha = \mu_2^\beta$$

⇔ Common tangent

• Liquidus, solidus and solvus determinations

Considering a binary system A-B: α (G^α) and β (G^β) two solid phases and **l** (G^l) liquid phase
For each temperature, the common tangent between G^α and G^l or between G^α and G^β give the compositions of the two phases in equilibrium:

Considering G^α or G^β, and G^l

⇨ X_e^α or X_e^β X_e^l

—— Solidus —— Liquidus

Considering G^α and G^β

⇨ X_e^α X_e^β

—— Solvus —— Solvus

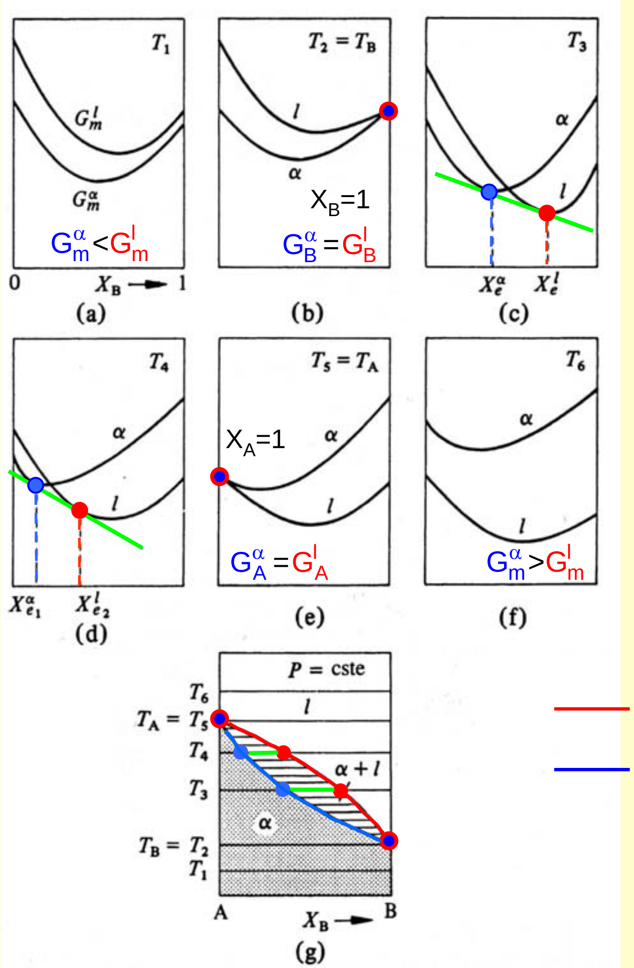
- **Binary systems**: determinations of the liquidus and solidus

Chemical potentials and common tangent construction (2/4)

- **Total miscibility of A and B**

↳2 phases α: solid ↔ $G_m^\alpha(X,T)$

l: liquid ↔ $G_m^l(X,T)$



liquidus

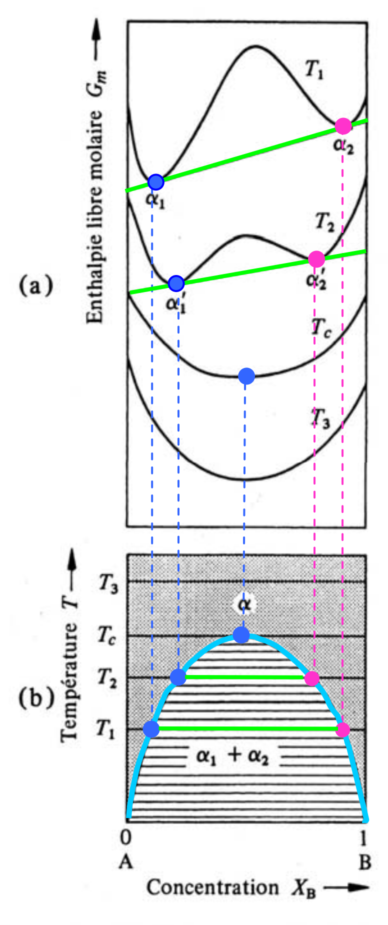
solidus

“Isomorphous”

- **Gap of miscibility in the solid state**

1 phase, α: solid $G_m^\alpha(X,T)$

α_1 and α_2: same crystal structure



$T<T_c$
Phase demixing

solvus

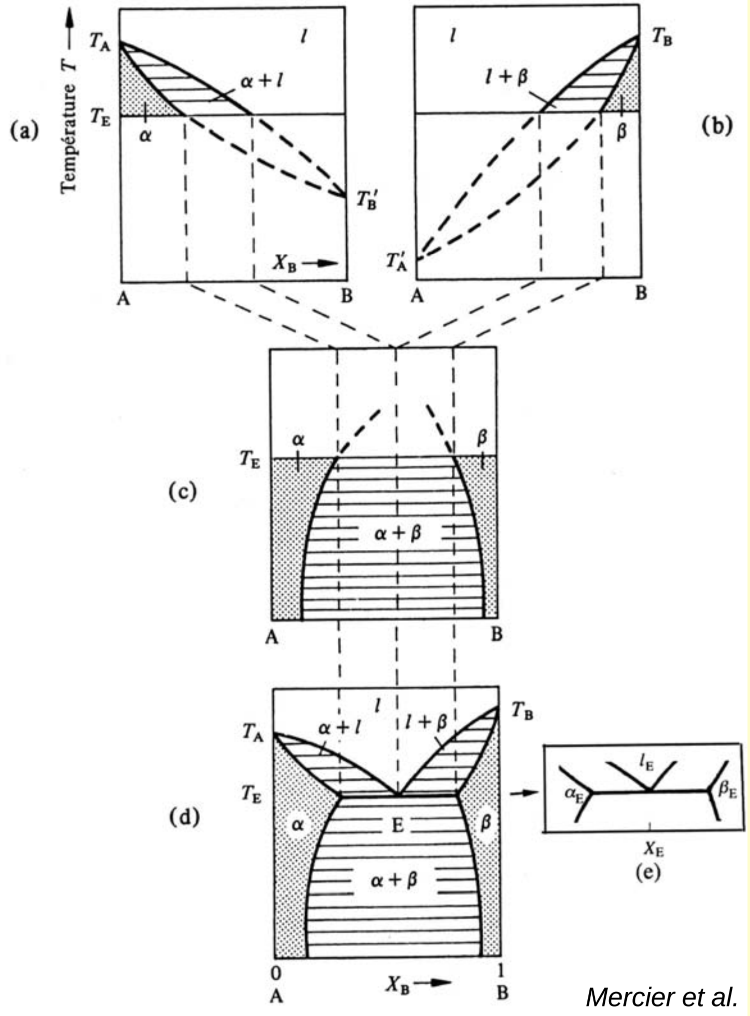
Mercier et al.

- **Binary systems**: determinations of the liquidus and solidus

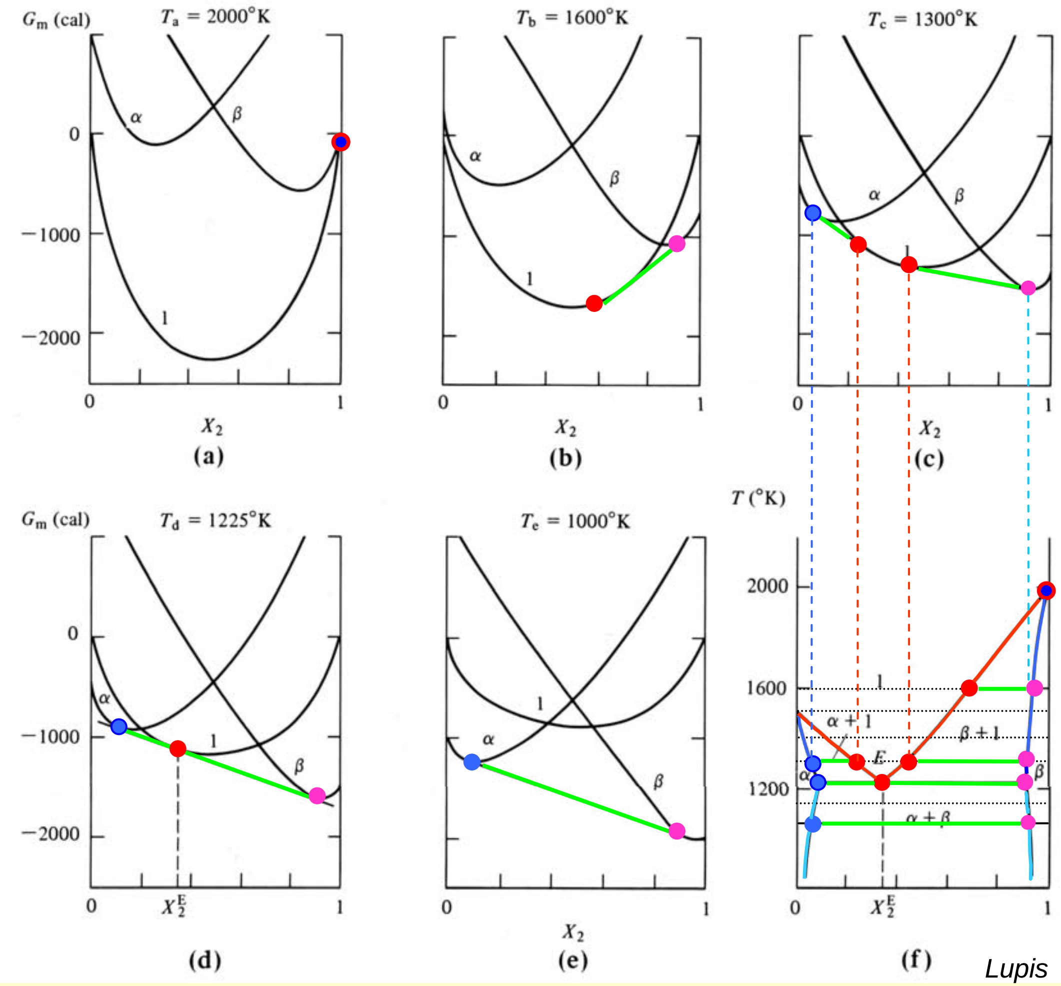
Chemical potentials and common tangent construction (3/4)

- **Eutectic point:** 3 phases, α and β two solid phases and l liquid phase

α and β: different crystal structures



Mercier et al.



Lupis

— liquidus — solidus — solvus

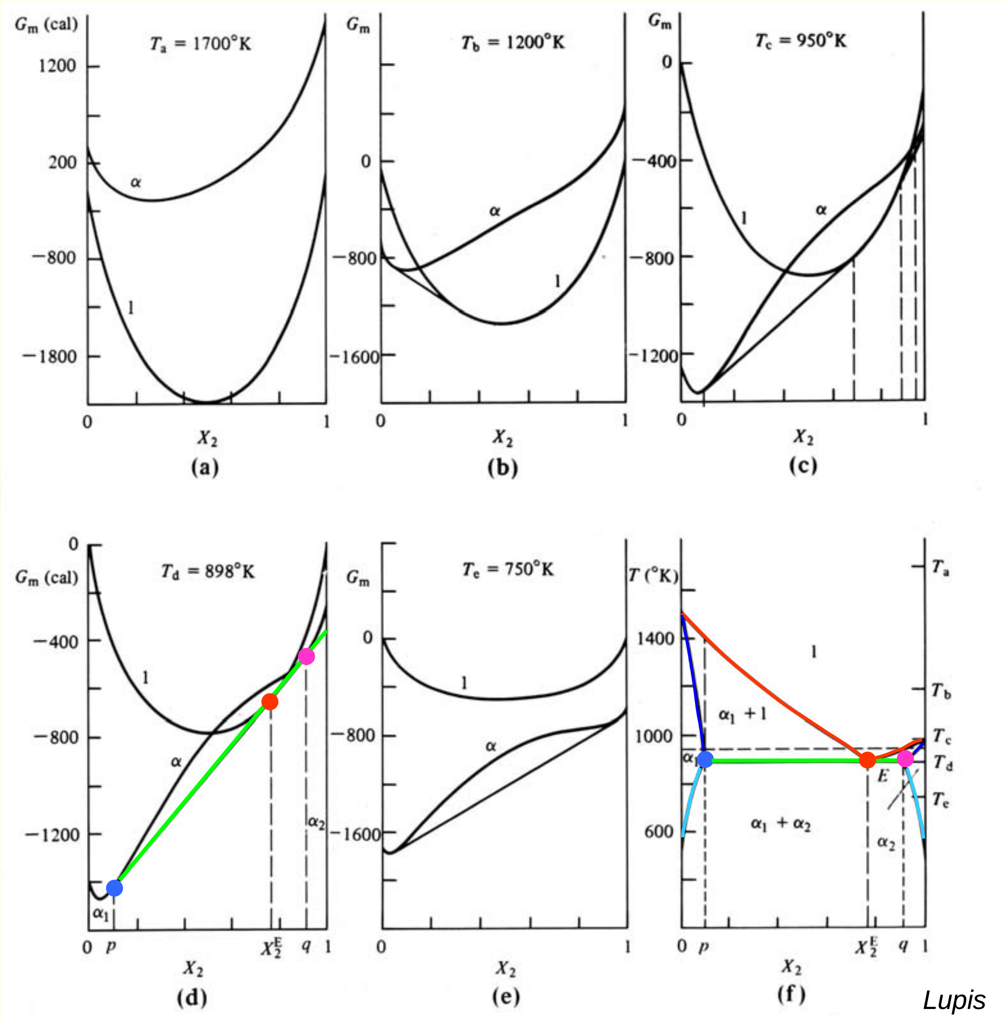
- **Binary systems**: determinations of the liquidus and solidus

Chemical potentials and common tangent construction (4/4)

- **Eutectic point:** 2 phases, α solid phase and l liquid phase

α_1 and α_2: same crystal structures

“Eutectic”



Lupis

Conclusion

How to calculate a binary phase diagram?

- **First step:** in the studied range of temperature and composition, it is absolutely necessary to have a preliminary knowledge of

- the nature of the several phases:
    - solid solutions,
    - defined compounds
- the possible presence of miscibility gap
- and for each phase, the description of $G_m(X,T)$

Part 2

- **Second step**: minimisation of the Gibbs free energy

Determination of the different boundaries lines (solvus, solidus and liquidus) by searching the equilibrium conditions.

☞ for a binary system with two phases in equilibrium

equilibrium condition ↔ searching for the two components the equality of the chemical potentials

Graphical method ⇔ comment tangent construction
Calculation method ⇔ Gibbs energy minimisation process

Part 3

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- Pure species or stoichiometric compounds

Polynomial function for the Gibbs energy:

Form used by the Scientific Group ThermoData Europe (SGTE):

$$\boxed{G_m(T) - H_m^{SER} = a + bT + cT\ln T + \sum_{2}^{n} d_n T^n}$$

Gibbs energy relative to a standard element reference state (SER), where H_m^{SER} is the enthalpy of the element or substance in its defined reference state at 298,15K

with $C_P = -T \left.\frac{\partial^2 G}{\partial T^2}\right|_P$

and the physical hypothesis of a linear variation of C_p:
$G = a + bT + cT\ln T + dT^2 \leftrightarrow C_p = -c - 2dT$

The other terms are probably added in order to have a better refinement with the experimental data

- Binary mixtures. Determination of the free energy change due to mixing

$$G_m = \underbrace{\sum_i G^{pure}}_{\substack{\text{pure components}\\ \text{in their reference states}\\ G^{ref}}} + \underbrace{G^{mix}}_{\substack{\text{free energy change}\\ \text{due to mixing}}} = \sum_i x_i G^\circ_i + \underset{?}{\boxed{G^{mix}}}$$

A and B are quasi-identical atoms (1/3) Ideal model

- **No chemical interaction** between A and B

❶ AA, BB and AB energy bonds are supposed identical → $H^{mix} = 0$

❷ Random mixing of atoms → configurational entropy S^{mix}

$$S^{mix} = k \log_e W = k \ln(N!/n_A!n_B!)$$ (k: Boltzamm's constant and W number of configurations)

$$S^{mix} = -R(x_A \log_e(x_A) + x_B \log_e(x_B))$$ (using Stirling's approximation)

$$\longrightarrow \quad G^{mix} = \cancel{H^{mix}} - TS^{mix} = RT\sum_i x_i \log_e(x_i)$$

$$\boxed{G_m = \underbrace{\sum_i x_i.G_i^o}_{G^{ref}} + \underbrace{R.T.\sum_i x_i.Log_e(x_i)}_{G^{mix}_{ideal}}}$$

- Binary mixtures. Determination of the free energy change due to mixing

A and B are quasi-identical atoms

(2/3) Non Ideal or excess models of Redlish-Kister
Regular solution

- **Chemical interaction** between A and B (pairwise interactions)

$$G_m = G^{ref} + G^{\substack{mix\\ideal}} + G^{\substack{mix\\excess}} \; ?$$

Model based on the Braggs Williams approach

❶ AB bond energies are different from the AA and BB bond energies

$\rightarrow H^{mix} = H^{\substack{mix\\excess}} \neq 0$

$\rightarrow$ Introduction of a parameter (L_{AB}) for each pair of constituents, called interaction energy

❷ Random mixing of the atoms → configurational entropy $= S^{\substack{mix\\ideal}}$

❸ Mixing entropy whose source is supposed entirely configurational $S^{\substack{mix\\excess}} = 0$

- **Interaction independent of the composition**

$$\boxed{G_m = \underbrace{\sum_i x_i.G_i^o}_{G^{ref}} + \underbrace{R.T.\sum_i x_i.Log_e\left(x_i\right)}_{G^{\substack{mix\\ideal}}} + \underbrace{\sum_i \sum_{j>i} x_i.x_j.L_{ij}}_{G^{\substack{mix\\excess}}}}$$

with L_{ij} depending or not of T

$$L_{ij} = A_{ij} + B_{ij}.T + \ldots$$

- Binary mixtures. Determination of the free energy change due to mixing

A and B are quasi-identical atoms

(2/3) Non Ideal or excess models of Redlich Kister
Non or Sub-Regular solution

- **Chemical interaction** between A and B **dependent of the composition**

$$G_m = \underbrace{\sum_i x_i.G_i^o}_{G^{ref}} + \underbrace{R.T.\sum_i x_i.\mathrm{Log}_e\left(x_i\right)}_{G^{\substack{mix\\ idéal}}} + \underbrace{\sum_i \sum_{j>i} x_i.x_j.(L^i_{ij}.x_i + L^j_{ij}.x_j)}_{G^{\substack{mix\\ excess}}}$$

Excess model of Redlish-Kister model: generalisation

$$G_m = \underbrace{\sum_i x_i.G_i^o}_{G^{ref}} + \underbrace{R.T.\sum_i x_i.\mathrm{Log}_e\left(x_i\right)}_{G^{\substack{mix\\ idéal}}} + \underbrace{\sum_i \sum_{j>i} x_i.x_j.\ \overbrace{\sum_\nu L_{ij}^{(\nu)}.\left(x_i - x_j\right)^\nu}^{\text{Redlich-Kister polynom: } L_{ij}}}_{G^{\substack{mix\\ excess}}}$$

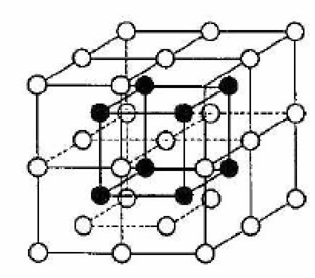
$$L_{ij}^{(\nu)} = A_{ij}^{(\nu)} + B_{ij}^{(\nu)}.T + \ldots$$

ν=0 ↔ **Regular solution**: L_{ij} depending of the temperature

ν=1 ↔ **Non or sub-regular solution**: L_{ij} depending also of the temperature **and** the composition

- Binary mixtures. Determination of the free energy change due to mixing

A and C are not quasi-identical atoms Sublattice model



- A and C can not mix: we consider two sublattices (A):(C)

In each sublattice (s), various quasi-identical atoms can mix, such as:

- (A,B):(C) or (A,B):(C,D) or (A,B…):(Va,C,D…) (Va, vacancy)
- $(A,B\ldots)_u:(Va,C,D)_v$ with $u^s = n^s / N^s$ site fraction associated to the sublattice s

❶ In each sublattice, chemical interaction: ideal or excess model

❷ In each sublattice: random mixing of the atoms → conf. entropy S^{mix}

☞ Introduction of the site fractions

$$y_i^s = \frac{n_i^s}{n_{va}^s + \sum_i n_i^s} = \frac{n_i^s}{N^s} \quad \Leftrightarrow \quad x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{va}^s)}$$

y_i^s site fraction of component i on sublattice s

n_i^s number of moles of component i on sublattice s

n_{Va}^s number of vacancies on sublattice s

N^S total number of sites in sublattice s

$$\boxed{G_m = \underbrace{\sum_i \sum_j y_i . y_j . G^o_{i:j}}_{G^{ref}} + \underbrace{R.T.\sum_s u^s \sum_i y_i^s . \mathrm{Log}_e\left(y_i^s\right)}_{G^{mix}_{ideal} = -T.S^{mix}_{ideal}} + \underbrace{\sum_s \sum_i \sum_{j>i} y_i^s . y_j^s . \sum_\nu L_{ij}^{s(\nu)} . \left(y_i^s - y_j^s\right)^\nu}_{G^{mix}_{excess} = H^{mix}_{excess}}}$$

SOLID PHASES. Solid solutions

Common models for solutions phases for the composition dependence:

- A and B are quasi-idendical:

\- Regular Solution Model – Excess model of Redlich-Kister (Redlich-Kister 1948)

- A and B are different:

\- Sublattice Model or the so-called Compound Energy Model
(Sundman and Agren 1981; Andersson 1986; Hillert 2001)

LIQUID PHASES.

- The most common used model: Excess model of Redlish-Kister

Ex: Cu-Ni: sub-regular solution
Ex: Fe-Cr: regular solution

- Other models developed in more specified cases

Ex: for oxide liquids (short-distance order)

\- Two-Sublattice Ionic Liquid Model (Hillert 1985; Sundman 1991)
\- Associate Model (Sommer 1982)
\- Kapoor-Frohberg-Gaye Cell Model (Gay 1984)
\- Quasi-Chemical Model of ionic liquid (Pelton 1986)

Refinement strategy

1. Polynomial functions of the end members are always supposed well known.
   All the phases of the diagram must be known

2. A thermodynamic model is chosen for each unknown phase of the diagram.
   This defines a set of of unknown model parameters (interaction parameters L)

3. A critical set of thermodynamic data
   ↳ from literature data or experimental measurements
   is chosen for each unknown phase

4. Refinements (least-square method) of the model parameters on the thermodynamic data and equilibrium calculations

↳ G(x,T) thermodynamic polynomial function → database

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Thermo-Calc software

THERMODYNAMIC DATABASES G(X,T)

+

CALPHAD formalism

1. First case:
All the phases of the diagrams ARE in the database.
➥ Calculation of the phase diagram by energy minimisation process

Examples: Cu-Ni, Fe-Cr

2. Second case:
All the phases of the diagram ARE NOT in the database.
➥ Assessment of the phase diagram by the refinement strategy

Thermo-Calc sofware

Structure of the Thermo-Calc software: the 6 basic modules in daily use

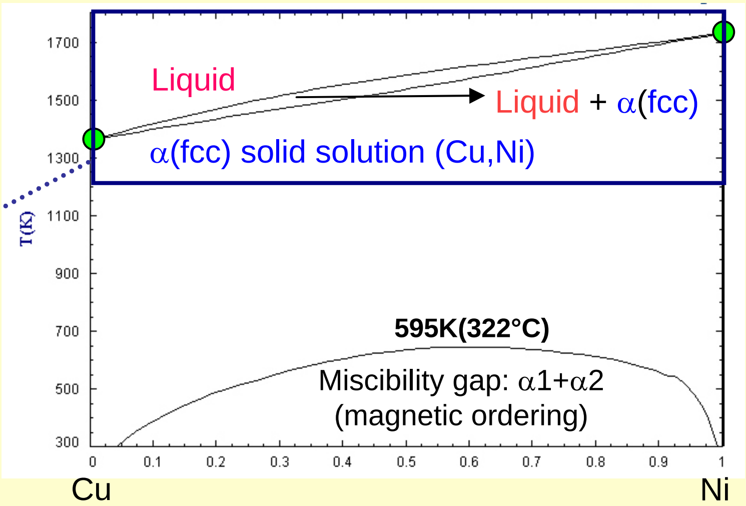
SYS	**S**ystem **U**tilities
TDB	**T**hermodynamic **D**ata**B**ase: thermodynamic data retrieval
GES	**G**ibbs **E**nergy **S**ystem: thermodynamic phase descriptions (models)
TAB	**Tab**ulation: tabulate thermodynamic functions
POLY	Equilibrium Calculation
POST	**Post**-Processor: plotting phase diagrams

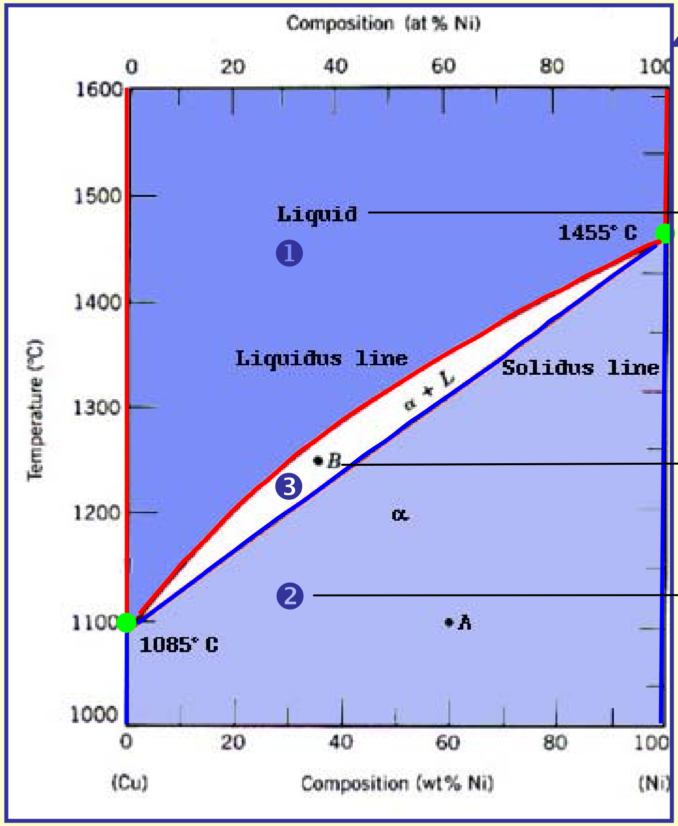
Cu-Ni: Total miscibility in the solid and liquid states

Features of the experimental known phase diagram

Pure Cu: α (fcc) $\xrightarrow{T_m=1085°C(1358K)}$ liquid

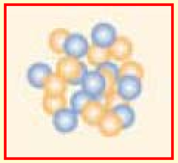
Pure Ni: α (fcc) $\xrightarrow{T_m=1455°C(1728K)}$ liquid





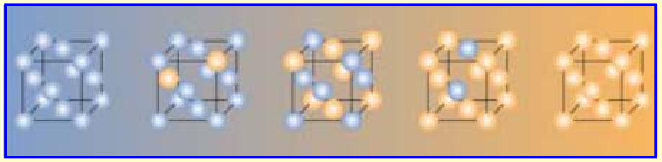
Cu-Ni. Experimental phase diagram between above 1000°C

❶ Total miscibility of Cu and Ni in the liquid L



❸ Coexistence of the two phases α and L

❷ Total miscibility of Cu and Ni in the solid phase α



Pure Cu - Mixture: total miscibility - Pure Ni

Cu-Ni: Total miscibility in the solid and liquid states

Description of the phases in the database. Models and values of the parameters (1/3)

● Which thermodynamic database?

“SSOL2” which contains Cu and Ni elements and the two phases
- Liquid phase: “Liquid”
- α(fcc) phase: “FCC_A1”

● Which models are used?

✓ Liquid: Excess model of Redlish Kister. **Non-regular** solution

$$G_m = x_{Cu}.G^{liq}_{Cu} + x_{Ni}.G^{liq}_{Ni} + R.T.(x_{Cu}.Log_e\left(x_{Cu}\right) + x_{Ni}.Log_e\left(x_{Ni}\right)) + x_{Cu}.x_{Ni}(L^{\circ}_{CuNi} + L^{1}_{CuNi}(x_{Cu} - x_{Ni})^{1})$$

✓ FCC_A1: Solid solution

Sublattice model: 1^{st} sublattice with Cu and Ni, 2^{nd} sublattice with vacancy: Cu,Ni:Va

$$G_m = y^{1}_{Cu}.G^{fcc}_{Cu:Va} + y^{1}_{Ni}.G^{fcc}_{Ni:Va} + R.T.(y^{1}_{Cu}.Log_e\left(y^{1}_{Cu}\right) + y^{1}_{Ni}.Log_e\left(y^{1}_{Ni}\right)) + y^{1}_{Cu}.y^{1}_{Ni}(L^{\circ}_{CuNi} + L^{1}_{CuNi}(y^{1}_{Cu} - y^{1}_{Ni})^{1})$$

Thermo-Calc exercise

How can I extract the values of the thermodynamic parameters ?
Handle the TDB and GES modules

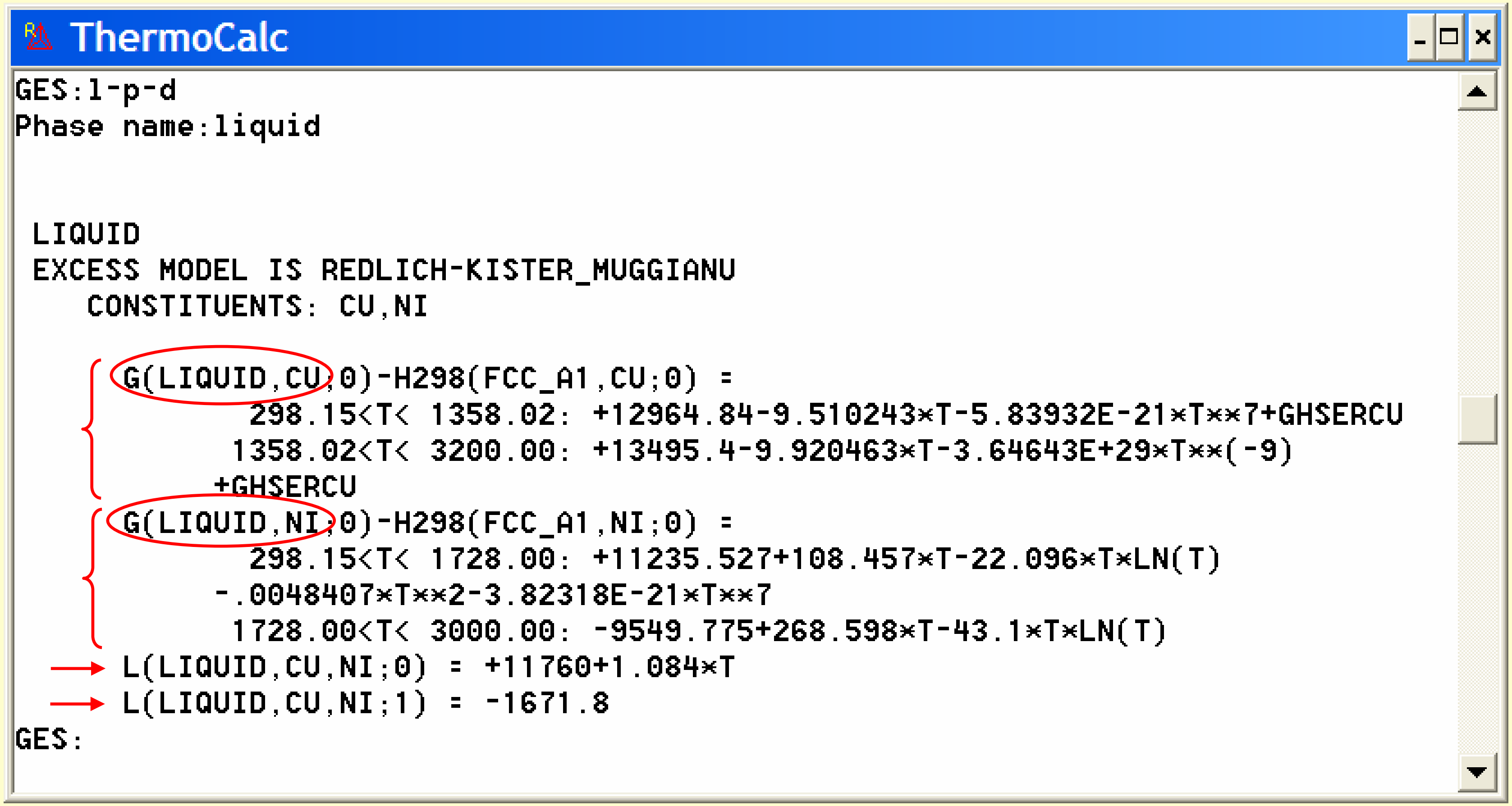
☞ cf. the annexe document
EXAMPLE 1
Calculation of the Cu-Ni phase diagram between 1000 and 1600°C
Exercice 1: SELECTING THE THERMODYNAMIC FUNCTIONS (TDB and GES modules)

3.2. Demonstrations and working examples: First case

Description of the phases in the database. Models and values of the parameters (2/3)

✓ Liquid: Excess model of Redlish Kister. **Non-regular** solution

$$G_m = x_{Cu}.G^{liq}_{Cu} + x_{Ni}.G^{liq}_{Ni} + R.T.(x_{Cu}.Log_e(x_{Cu}) + x_{Ni}.Log_e(x_{Ni})) + x_{Cu}.x_{Ni}(L^{\circ}_{CuNi} + L^{1}_{CuNi}(x_{Cu} - x_{Ni})^1)$$



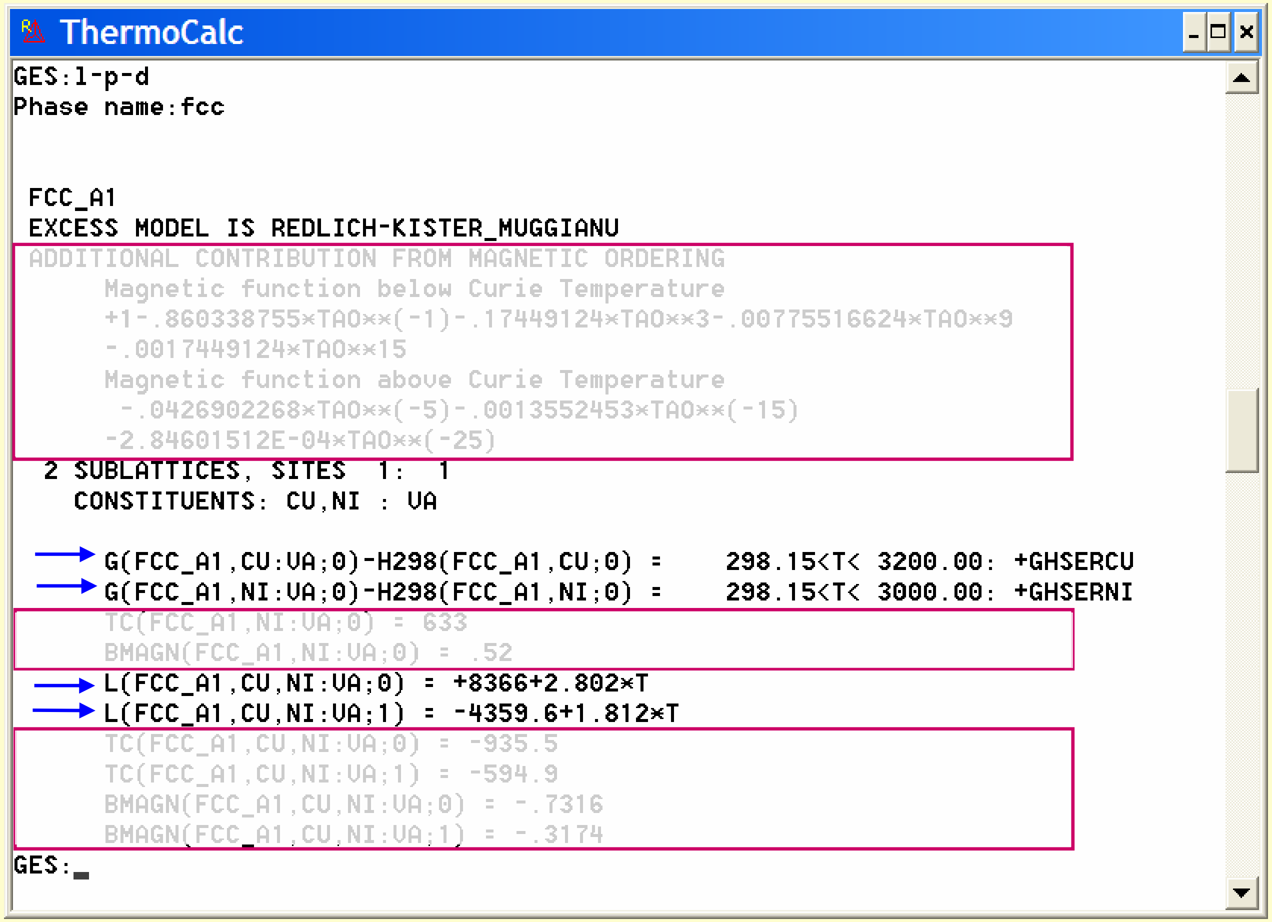
```
GES:l-p-d
Phase name:liquid


 LIQUID
 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU
    CONSTITUENTS: CU,NI

      G(LIQUID,CU;0)-H298(FCC_A1,CU;0) =
             298.15<T< 1358.02: +12964.84-9.510243*T-5.83932E-21*T**7+GHSERCU
            1358.02<T< 3200.00: +13495.4-9.920463*T-3.64643E+29*T**(-9)
           +GHSERCU
      G(LIQUID,NI;0)-H298(FCC_A1,NI;0) =
             298.15<T< 1728.00: +11235.527+108.457*T-22.096*T*LN(T)
           -.0048407*T**2-3.82318E-21*T**7
            1728.00<T< 3000.00: -9549.775+268.598*T-43.1*T*LN(T)
      L(LIQUID,CU,NI;0) = +11760+1.084*T
      L(LIQUID,CU,NI;1) = -1671.8
GES:
```

Description of the phases in the database. Models and values of the parameters (3/3)

✓ FCC_A1: Solid solution

Sublattice model: 1st sublattice with Cu and Ni, 2nd sublattice with vacancy: (Cu,Ni):(Va) ↔ $y_{Va} = 1$

$$G_m = y^1_{Cu} G^{fcc}_{Cu:Va} + y^1_{Ni} G^{fcc}_{Ni:Va} + R.T.(y^1_{Cu}.Log_e\left(y^1_{Cu}\right) + y^1_{Ni}.Log_e\left(y^1_{Ni}\right)) + y^1_{Cu}.y^1_{Ni}({}^{\circ}L_{CuNi} + {}^{1}L_{CuNi}(y^1_{Cu} - y^1_{Ni})^1)$$

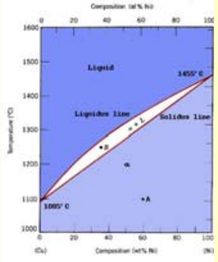


```
GES:l-p-d
Phase name:fcc


 FCC_A1
 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU
 ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING
      Magnetic function below Curie Temperature
      +1-.860338755*TAO**(-1)-.17449124*TAO**3-.00775516624*TAO**9
      -.0017449124*TAO**15
      Magnetic function above Curie Temperature
       -.0426902268*TAO**(-5)-.0013552453*TAO**(-15)
      -2.84601512E-04*TAO**(-25)
  2 SUBLATTICES, SITES  1:  1
    CONSTITUENTS: CU,NI : VA

      G(FCC_A1,CU:VA;0)-H298(FCC_A1,CU;0) =    298.15<T< 3200.00: +GHSERCU
      G(FCC_A1,NI:VA;0)-H298(FCC_A1,NI;0) =    298.15<T< 3000.00: +GHSERNI
      TC(FCC_A1,NI:VA;0) = 633
      BMAGN(FCC_A1,NI:VA;0) = .52
      L(FCC_A1,CU,NI:VA;0) = +8366+2.802*T
      L(FCC_A1,CU,NI:VA;1) = -4359.6+1.812*T
      TC(FCC_A1,CU,NI:VA;0) = -935.5
      TC(FCC_A1,CU,NI:VA;1) = -594.9
      BMAGN(FCC_A1,CU,NI:VA;0) = -.7316
      BMAGN(FCC_A1,CU,NI:VA;1) = -.3174
GES:_
```

Magnetic contribution terms are not useful in our studied range of T

Cu-Ni: Total miscibility in the solid and liquid states

Plotting the calculated phase diagram (1/2)



Thermo-Calc exercise

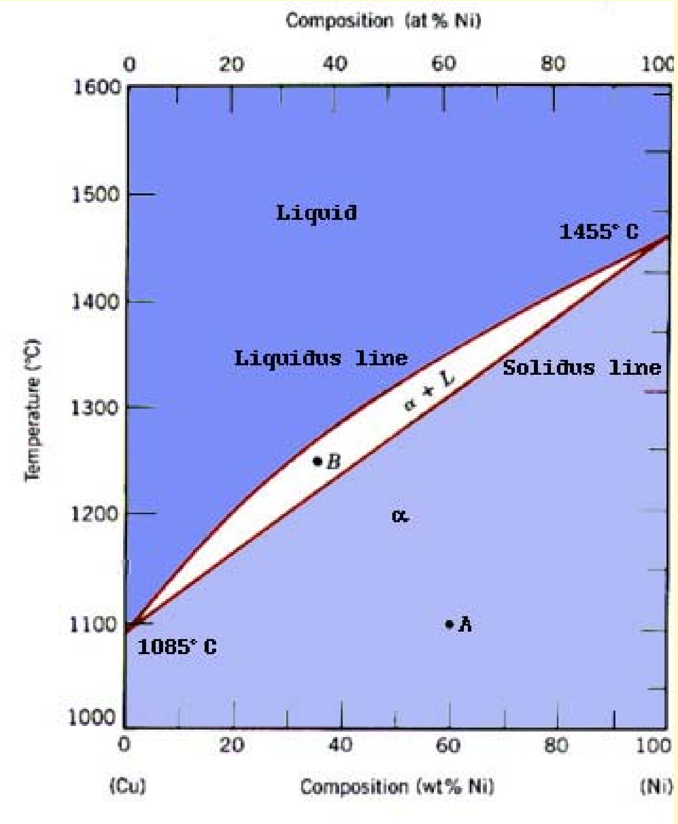
Calculate and plot by yourself the phase diagram
Handle the POLY and POST modules

☞ cf. the annexe document
EXAMPLE 1
Calculation of the Cu-Ni phase diagram between 1000 and 1600°C
Exercise 2. CALCULATING AND PLOTTING THE PHASE DIAGRAM (POLY and POST modules)

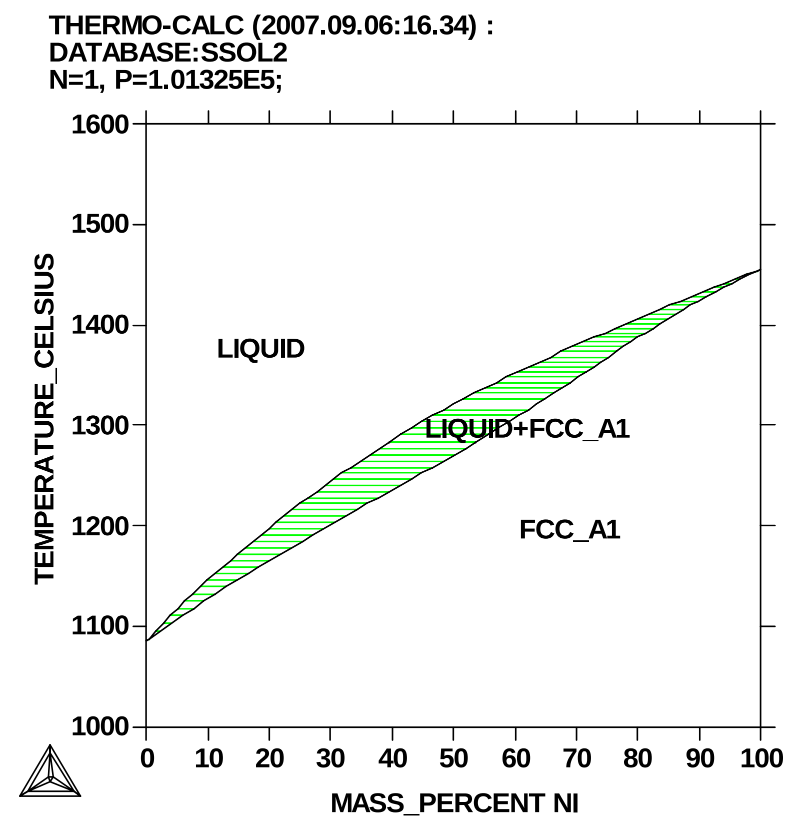
Cu-Ni: Total miscibility in the solid and liquid states

Plotting the calculated phase diagram (2/2)

Experimental phase diagram



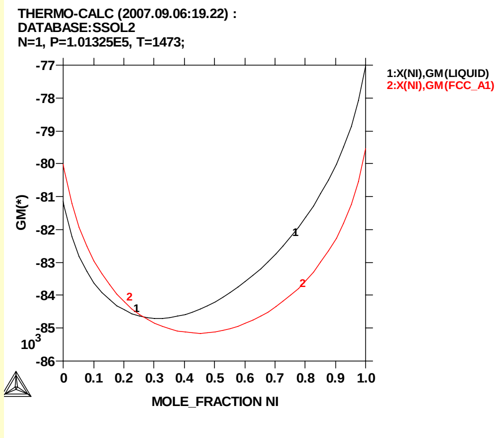
Calculated phase diagram



Comparison of the experimental and the calculated phase diagrams

Cu-Ni: Total miscibility in the solid and liquid states

Plotting the thermodynamic functions: Molar Gibbs energy curves (1/2)

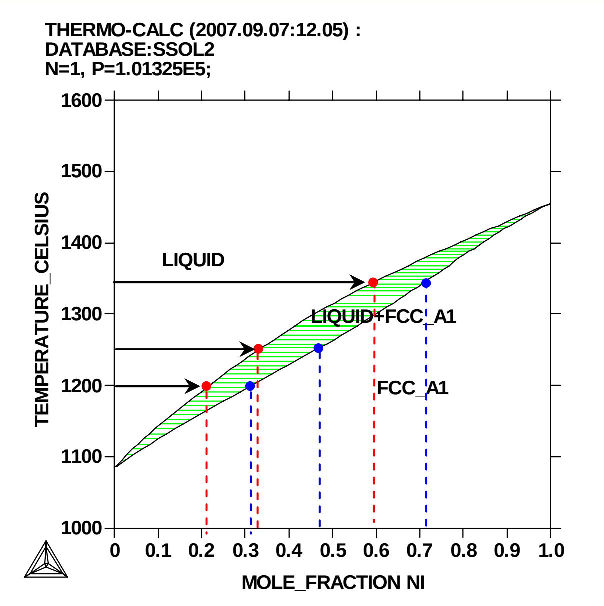


Thermo-Calc exercise

Plot by yourself the molar Gibbs energy curves
Handle the POLY and POST modules

☞ cf. the annexe document
EXAMPLE 1
Calculation of the Cu-Ni phase diagram between 1000 and 1600°C
Exercise 3. PLOTTING THE MOLAR GIBBS ENERGY CURVES G=f(X)

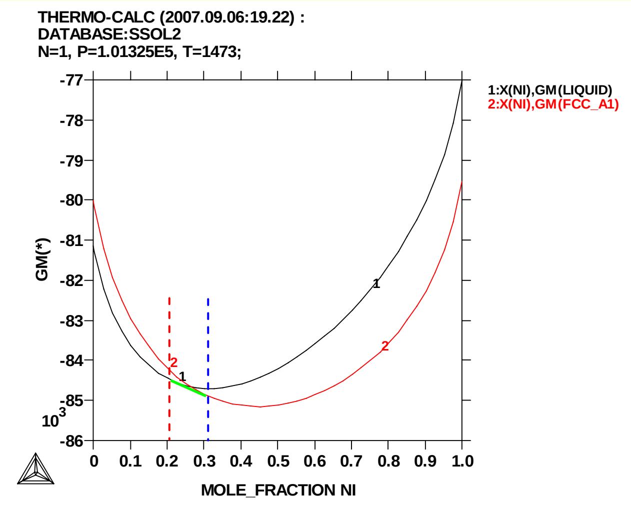
Plotting the thermodynamic functions (2/2)



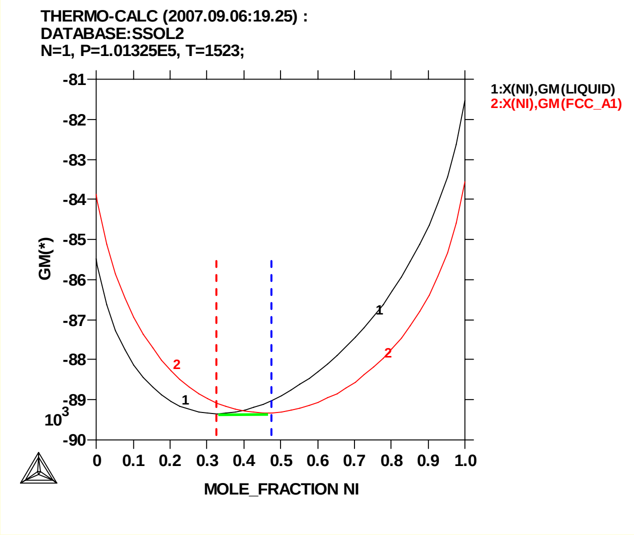
T=1623K=1350°C

T=1523K=1250°C

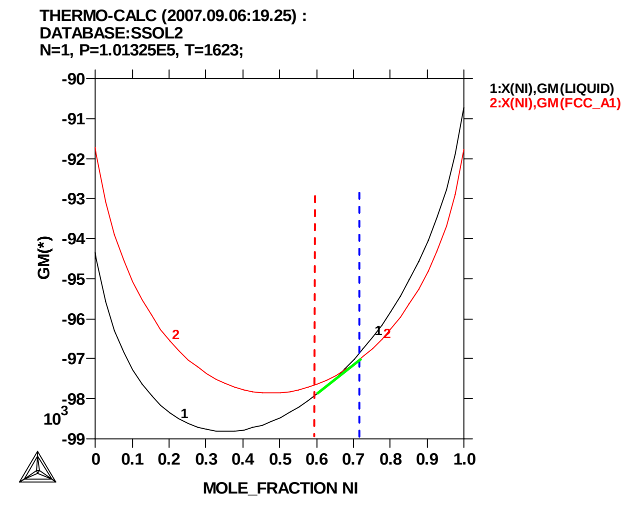
T=1473K=1200°C



T=1473K=1200°C



T=1523K=1250°C



T=1623K=1350°C

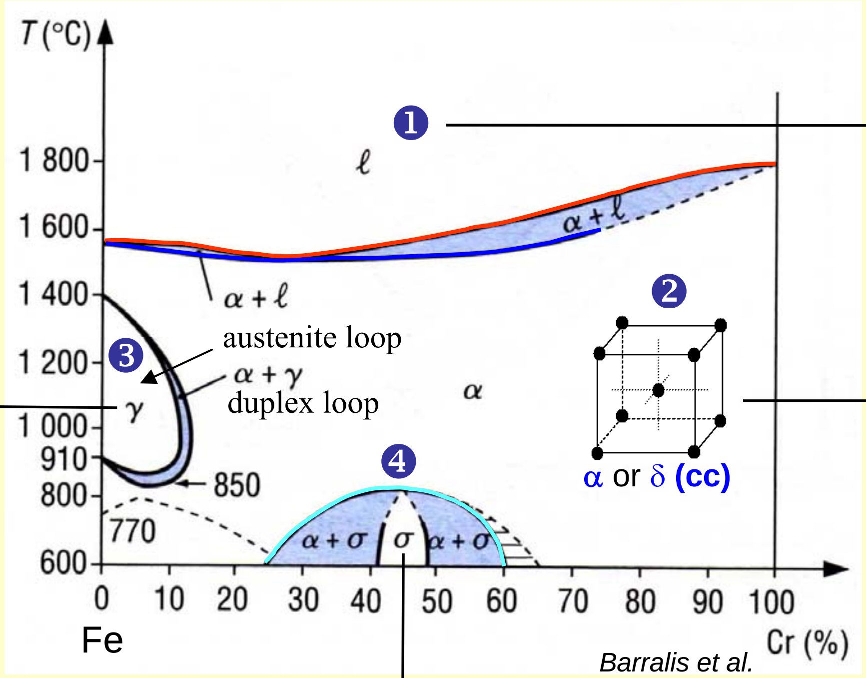
Fe-Cr: how to handle a miscibility gap

Features of the experimental known phase diagram

Pure Fe: α (cc) $\xrightarrow{T_m=912°C(1185K)}$ γ (cfc) $\xrightarrow{T_m=1394°C(1667K)}$ δ (cc) $\xrightarrow{T_m=1535°C(1808K)}$ liquid

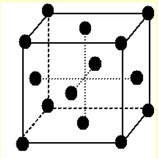
Pure Cr: α (fcc) $\xrightarrow{T_m=1800°C(2073K)}$ liquid

Azeotrope-type phase diagram



Barralis et al.

Total miscibility in liquid



γ (fcc)

γ solid solution in Fe-γ: “austenite”

α solid solution in Fe-α or Fe-δ: “ferrite”

Cr → “alphagene” element

σ intermediate phase (brittle phase)

↳ Miscibility gap in the solid state

Fe-Cr: how to handle a miscibility gap

Description of the phases in the database. Models and values of the parameters (1/5)

- **Which thermodynamic database?**

"PTERN" which contains Fe and Cr elements and the four phases

Liquid phase: "Liquid"
γ (fcc) phase: "FCC_A1"
α (cc) phase: "BCC_A2"
σ sigma phase: "SIGMA"

- **Which models are used?**

✓ Liquid: Excess model of Redlish Kister: **Regular** solution

✓ FCC_A1: Solid solution
Sublattice model: 1st sublattice with Fe and Cr, 2nd sublattice with vacancy: (Fe,Cr):(Va)

✓ BCC_A2: Solid solution
Sublattice model: 1st sublattice with Fe and Cr, 2nd sublattice with vacancy: (Fe,Cr):(Va)

✓ SIGMA: Solid solution
Sublattice model: 1st sublattice with Fe, 2nd sublattice with Cr, 3rd sublattice with Fe and Cr: (Fe):(Cr):(Fe,Cr)

Thermo-Calc exercise

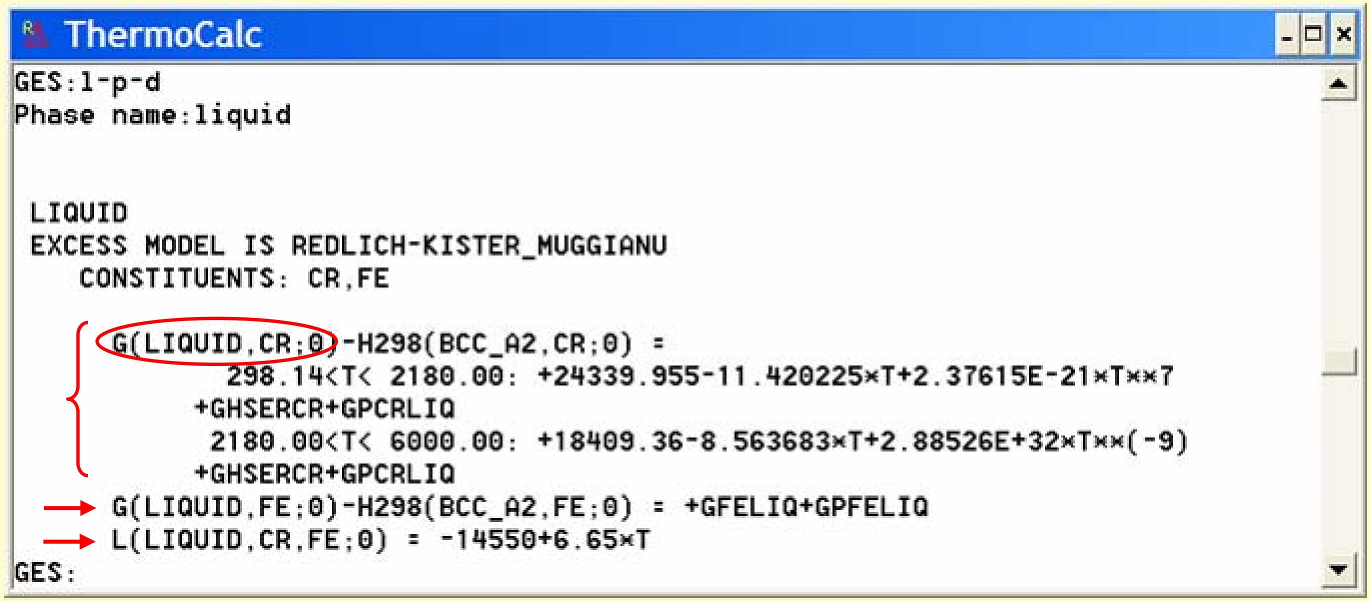
How to see the values of the thermodynamic parameters ?
Handle the TDB and GES modules

☞ cf. the annexe document
EXAMPLE 2
Calculation of the Fe-Cr phase diagram between 600 and 2200°C
Exercice 1. SELECTING THE THERMODYNAMIC FUNCTIONS (TDB and GIBBS modules)

Description of the phases in the database. Models and values of the parameters (2/5)

✓ Liquid: Excess model of Redlish Kister: **Regular** solution

$$G_m = x_{Cr}.G_{Cr}^{liq} + x_{Fe}.G_{Fe}^{liq} + R.T.(x_{Cr}.Log_e\left(x_{Cr}\right) + x_{Fe}.Log_e\left(x_{Fe}\right)) + x_{Cr}.x_{Fe}.\overset{\circ}{L}_{CrFe}$$



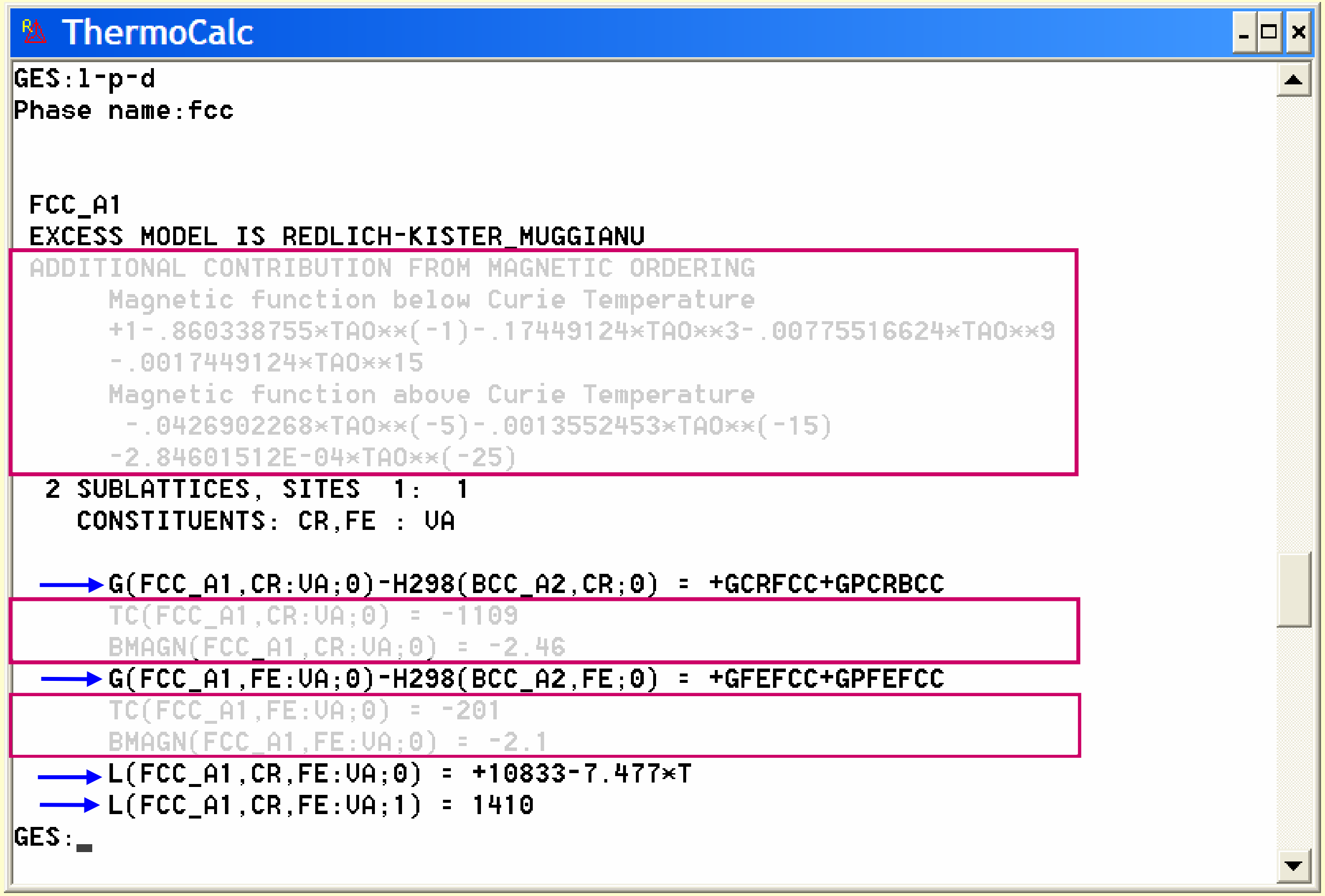
```
GES:l-p-d
Phase name:liquid


 LIQUID
 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU
    CONSTITUENTS: CR,FE

      G(LIQUID,CR;0)-H298(BCC_A2,CR;0) =
              298.14<T< 2180.00: +24339.955-11.420225*T+2.37615E-21*T**7
           +GHSERCR+GPCRLIQ
            2180.00<T< 6000.00: +18409.36-8.563683*T+2.88526E+32*T**(-9)
           +GHSERCR+GPCRLIQ
      G(LIQUID,FE;0)-H298(BCC_A2,FE;0) = +GFELIQ+GPFELIQ
      L(LIQUID,CR,FE;0) = -14550+6.65*T
GES:
```

Description of the phases in the database. Models and values of the parameters (3/5)

✓ FCC_A1: Solid solution

Sublattice model: 1st sublattice with Cr and Fe, 2nd sublattice with vacancy: (Cr,Fe):(Va) $\leftrightarrow y_{Va} = 1$

$$G_m = y^1_{Cr} G^{fcc}_{Cr:Va} + y^1_{Fe} G^{fcc}_{Fe:Va} + R.T.(y^1_{Cr}.Log_e\left(y^1_{Cr}\right) + y^1_{Fe}.Log_e\left(y^1_{Fe}\right)) + y^1_{Cr}.y^1_{Fe}(L^{\circ}_{CrFe} + L^1_{CrFe}(y^1_{Cr} - y^1_{Fe})^1)$$



```
GES:l-p-d
Phase name:fcc


 FCC_A1
 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU
 ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING
      Magnetic function below Curie Temperature
      +1-.860338755*TAO**(-1)-.17449124*TAO**3-.00775516624*TAO**9
      -.0017449124*TAO**15
      Magnetic function above Curie Temperature
       -.0426902268*TAO**(-5)-.0013552453*TAO**(-15)
      -2.84601512E-04*TAO**(-25)
  2 SUBLATTICES, SITES  1:  1
    CONSTITUENTS: CR,FE : VA

      G(FCC_A1,CR:VA;0)-H298(BCC_A2,CR;0)  = +GCRFCC+GPCRBCC
      TC(FCC_A1,CR:VA;0)  = -1109
      BMAGN(FCC_A1,CR:VA;0)  = -2.46
      G(FCC_A1,FE:VA;0)-H298(BCC_A2,FE;0)  = +GFEFCC+GPFEFCC
      TC(FCC_A1,FE:VA;0)  = -201
      BMAGN(FCC_A1,FE:VA;0)  = -2.1
      L(FCC_A1,CR,FE:VA;0)  = +10833-7.477*T
      L(FCC_A1,CR,FE:VA;1)  = 1410
GES:_
```

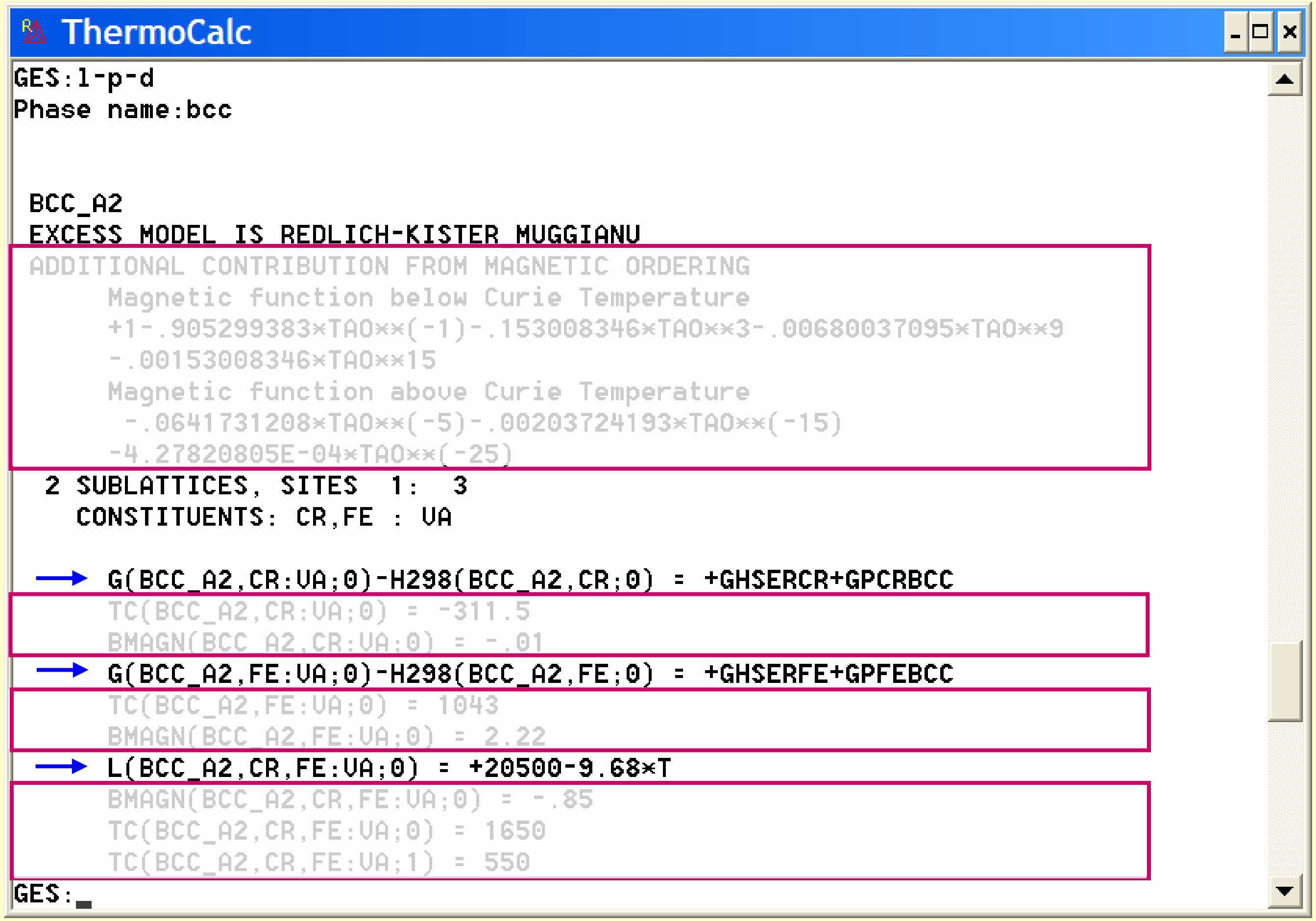
Magnetic contribution terms are not useful in our studied range of T

Description of the phases in the database. Models and values of the parameters (4/5)

✓ BCC_A2: Solid solution

Sublattice model: 1st sublattice with Cr and Fe, 2nd sublattice with vacancy: (Cr,Fe):(Va) $\leftrightarrow y_{Va} = 1$

$$G_m = y^1_{Cr}.\boxed{G^{bcc}_{Cr:Va}} + y^1_{Fe}.\boxed{G^{bcc}_{Fe:Va}} + R.T.(y^1_{Cr}.Log_e\left(y^1_{Cr}\right) + y^1_{Fe}.Log_e\left(y^1_{Fe}\right)) + y^1_{Cr}.y^1_{Fe}\boxed{\overset{\circ}{L}_{CrFe}}$$



```
GES:l-p-d
Phase name:bcc


 BCC_A2
 EXCESS MODEL IS REDLICH-KISTER MUGGIANU
 ADDITIONAL CONTRIBUTION FROM MAGNETIC ORDERING
      Magnetic function below Curie Temperature
      +1-.905299383*TAO**(-1)-.153008346*TAO**3-.00680037095*TAO**9
      -.00153008346*TAO**15
      Magnetic function above Curie Temperature
       -.0641731208*TAO**(-5)-.00203724193*TAO**(-15)
      -4.27820805E-04*TAO**(-25)
  2 SUBLATTICES, SITES  1:  3
    CONSTITUENTS: CR,FE : VA

 →   G(BCC_A2,CR:VA;0)-H298(BCC_A2,CR;0) = +GHSERCR+GPCRBCC
      TC(BCC_A2,CR:VA;0) = -311.5
      BMAGN(BCC_A2,CR:VA;0) = -.01
 →   G(BCC_A2,FE:VA;0)-H298(BCC_A2,FE;0) = +GHSERFE+GPFEBCC
      TC(BCC_A2,FE:VA;0) = 1043
      BMAGN(BCC_A2,FE:VA;0) = 2.22
 →   L(BCC_A2,CR,FE:VA;0) = +20500-9.68*T
      BMAGN(BCC_A2,CR,FE:VA;0) = -.85
      TC(BCC_A2,CR,FE:VA;0) = 1650
      TC(BCC_A2,CR,FE:VA;1) = 550
GES:_
```

Magnetic contribution terms are not useful in our studied range of T

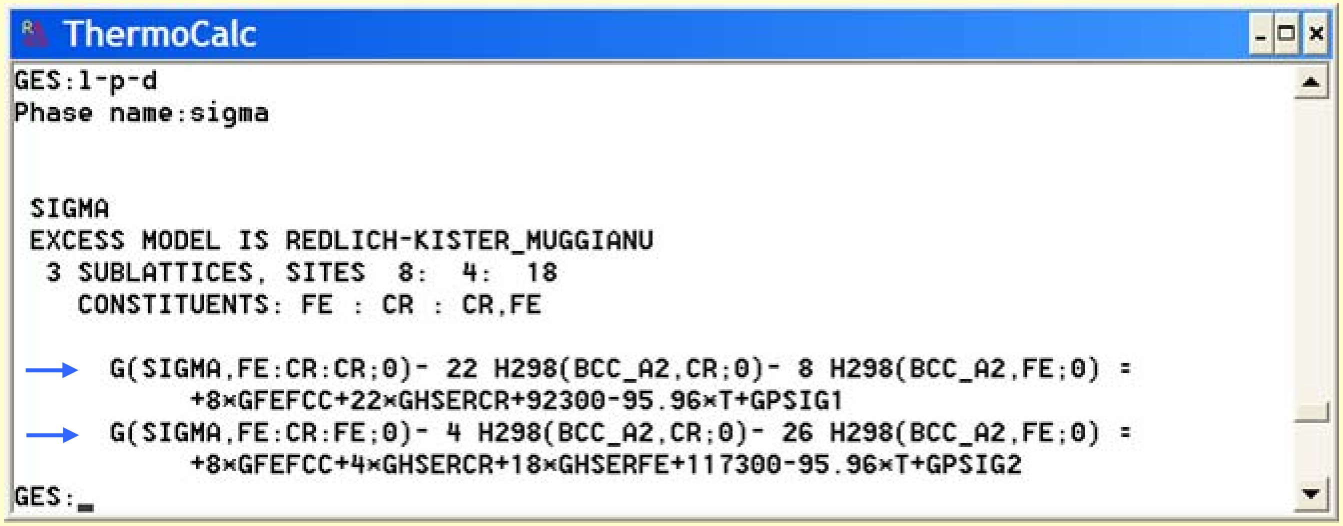
Description of the phases in the database. Models and values of the parameters (5/5)

✓ SIGMA: Solid solution

Sublattice model: 1st sublattice with Fe, 2nd sublattice with Cr, 3rd sublattice with Fe and Cr:

$(Fe)_8:(Cr)_4:(Cr,Fe)_{18} \leftrightarrow y^1_{Fe} = y^2_{Cr} = 1$

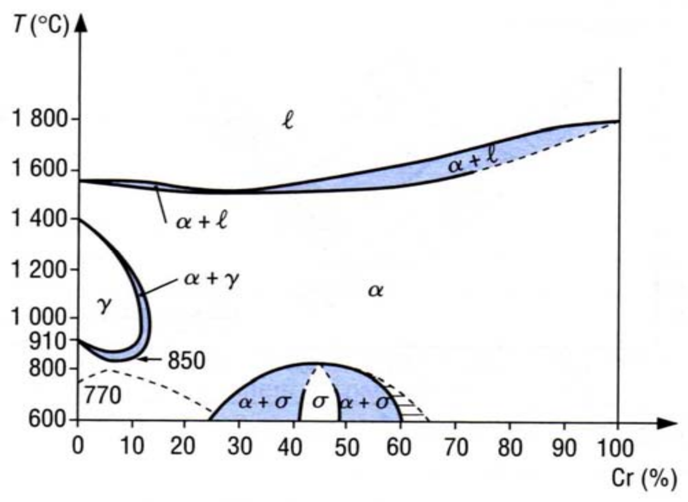
$$G_m = y^3_{Cr}.\boxed{G_{Fe:Cr:Cr}} + y^3_{Fe}.\boxed{G_{Fe:Cr:Fe}} + R.T.(18(y^3_{Cr}.Log_e\left(y^3_{Cr}\right) + y^3_{Fe}.Log_e\left(y^3_{Fe}\right)))$$



```
GES:l-p-d
Phase name:sigma


 SIGMA
 EXCESS MODEL IS REDLICH-KISTER_MUGGIANU
  3 SUBLATTICES, SITES  8:  4:  18
   CONSTITUENTS: FE : CR : CR,FE

→     G(SIGMA,FE:CR:CR;0)- 22 H298(BCC_A2,CR;0)- 8 H298(BCC_A2,FE;0) =
           +8*GFEFCC+22*GHSERCR+92300-95.96*T+GPSIG1
→     G(SIGMA,FE:CR:FE;0)- 4 H298(BCC_A2,CR;0)- 26 H298(BCC_A2,FE;0) =
           +8*GFEFCC+4*GHSERCR+18*GHSERFE+117300-95.96*T+GPSIG2
GES:_
```

Fe-Cr: how to handle a miscibility gap

Plotting the calculated phase diagram (1/2)



Thermo-Calc exercise

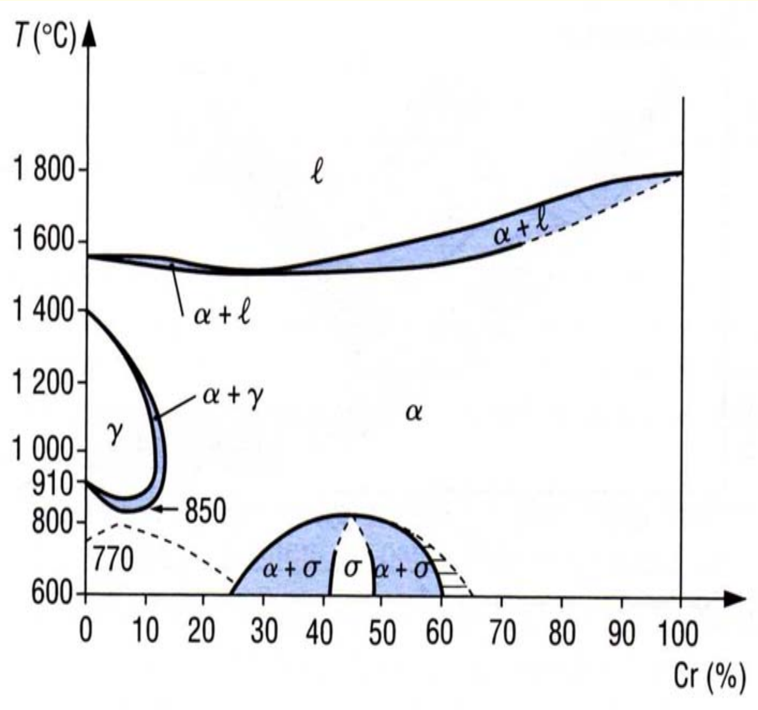
Calculate and plot by yourself the phase diagram
Handle the POLY and POST modules

☞ cf. the annexe document
EXAMPLE 2
Calculation of the Fe-Cr phase diagram between 600 and 2200°C
Exercice 2. CALCULATING AND PLOTTING THE PHASE DIAGRAM (POLY and POST modules)

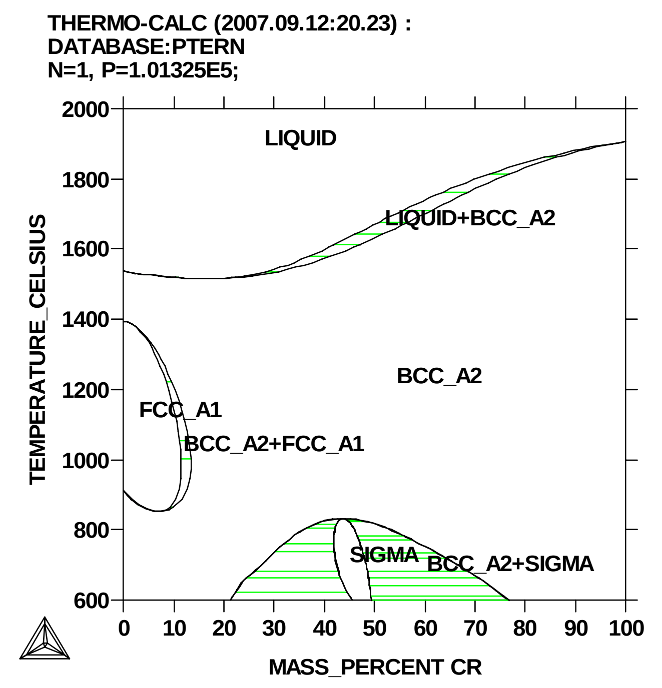
Fe-Cr: how to handle a miscibility gap

Plotting the calculated phase diagram (2/2)

Experimental phase diagram



Calculated phase diagram



Comparison of the experimental and the calculated phase diagrams

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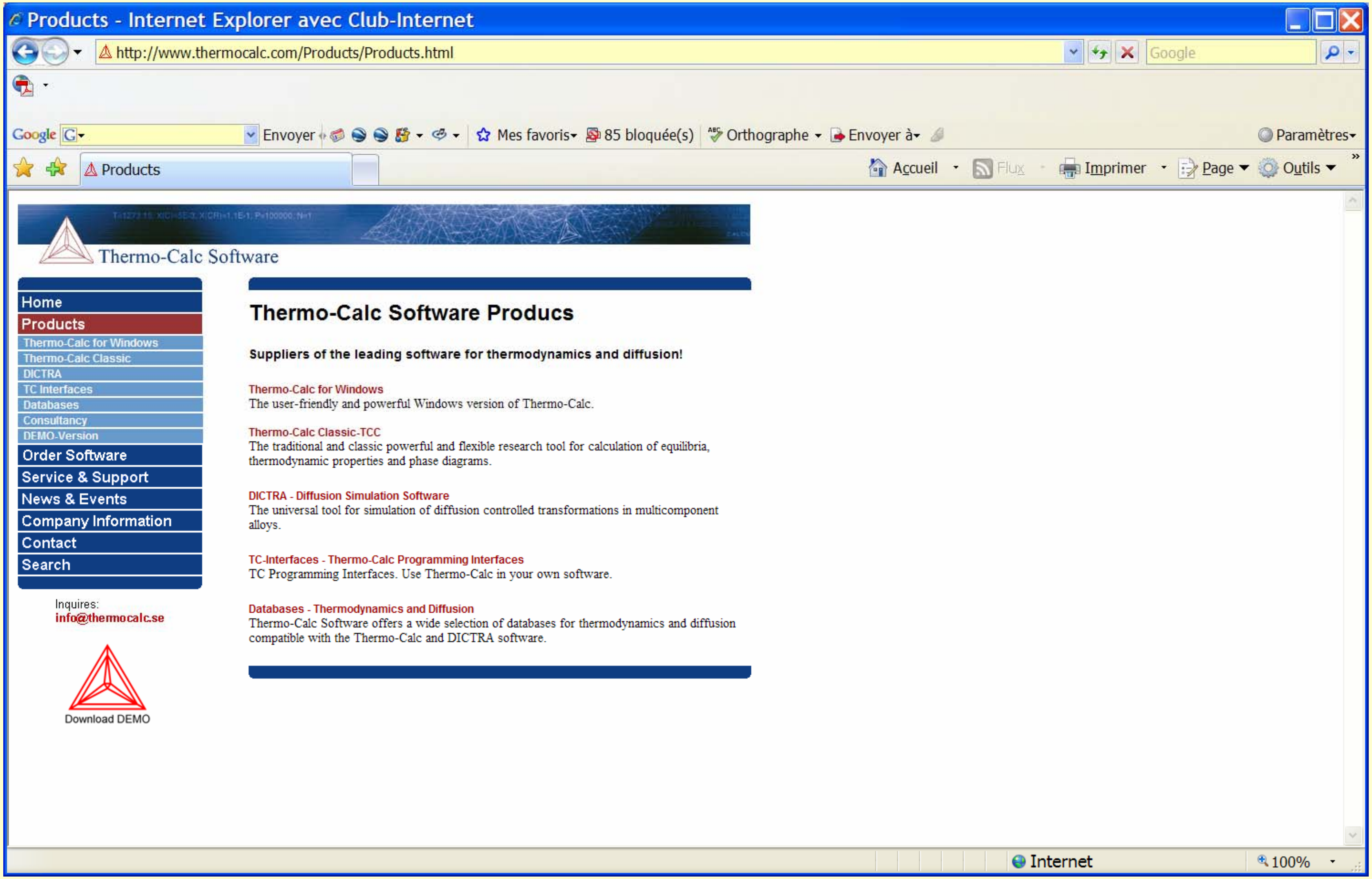
Thermo-Calc information



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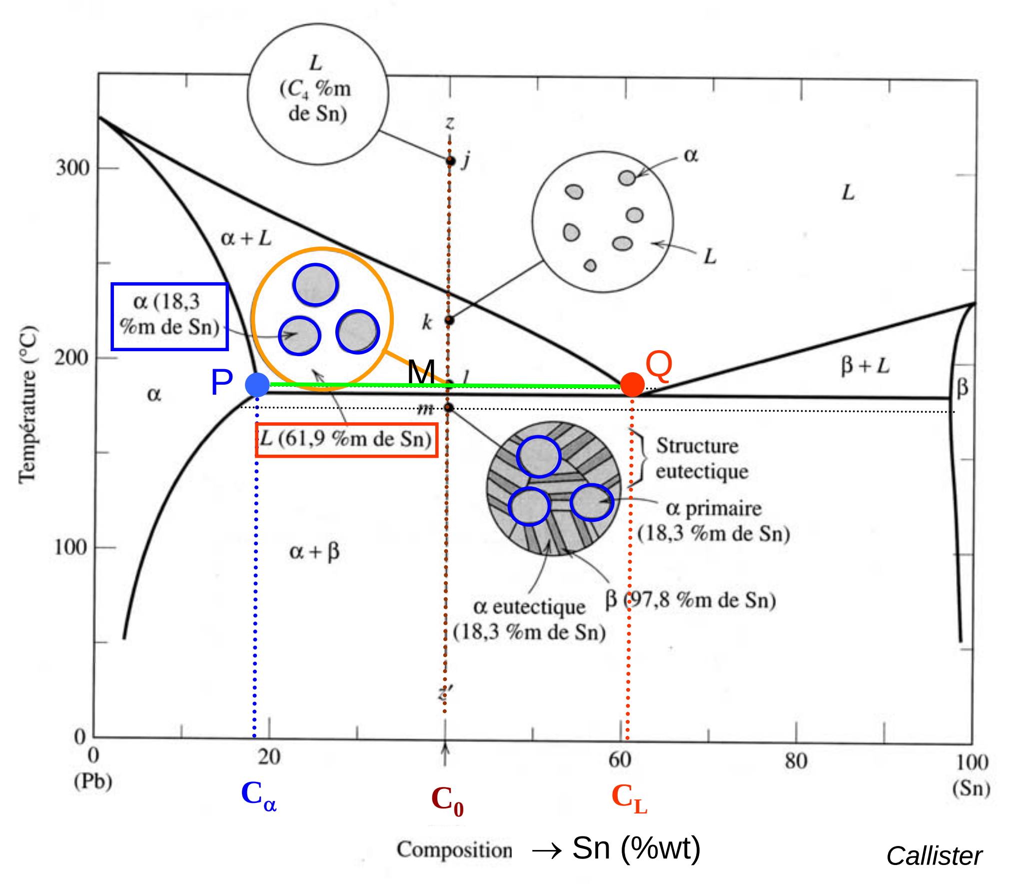
SUPPLEMENTS

Microstructure and phase diagram

Composition and proportion of the phases during the cooling of an liquid alloy

Exemple: Pb-Sn phase diagram

Variation of the composition of the phases during the cooling



Callister

Proportion of the phases

C_0: mass percent (%wt) of Sn in the alloy
C_α: mass percent (%wt) of Sn in α phase
C_L: mass percent (%wt) of Sn in L phase
f_α : mass percent (%) of the α phase
f_L : mass percent (%) of the L phase

$$\begin{cases} f_\alpha + f_l = 1 \\ f_\alpha C_\alpha + f_L C_L = C_0 \end{cases}$$

➯ "Level Rule"

For an alloy of concentration C_0

$$\boxed{f_\alpha = (C_L - C_0) / (C_L - C_\alpha) = MQ / PQ}$$

$$\boxed{f_L = (C_0 - C_\alpha) / (C_L - C_\alpha) = PM / PQ}$$

Gibbs Phase Rule

Variance (V) or number of degrees of freedom: number of independent variables

$$V = C + n - \phi$$

C: number of system components
n: number of variables which can vary (temperature, pressure, volume)
ϕ: maximum number of stable phases

Invariant equilibrium ↔ **V=0**: equilibrium attained only for a single set of values

☞ **One-component system**:

- 1 component → $C = 1$
- varying variables: temperature and pressure → $n = 2$

$\boxed{\hookrightarrow V = 3 - \phi}$

$\phi=3 \leftrightarrow$ **V=0** → **P,T fixed** ⇒ At most three coexisting phases for one single (P,T) couple (see triple point)

☞ **Binary system**:

- 2 components → $C = 2$ and $V = 2 + n - \phi$
- 1 variable, neglecting pressure and volume variations: P fixed (P=1 atm) → $n = 1$

$\boxed{\hookrightarrow V = 3 - \phi}$

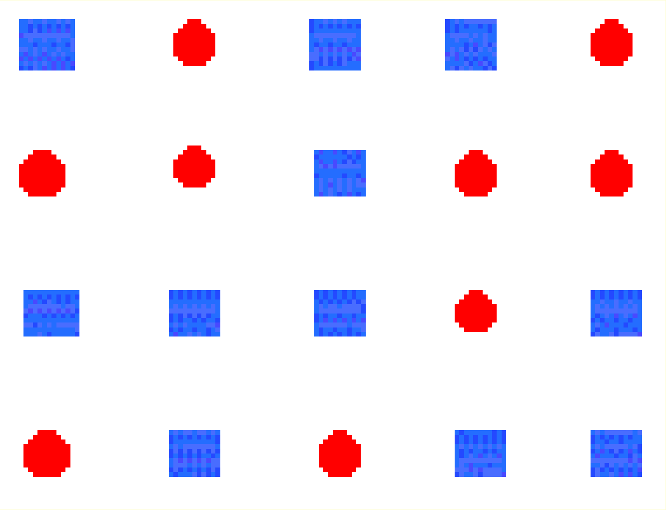
$\phi=3 \leftrightarrow$ **V=0** → **T fixed** ⇒ At most three coexisting phases for one single T_E called eutectic or peritectic temperature

Solid solutions: substitutional and interstitial solutions

● substitutional solid solution

The site of an atom A can be substituted by an atom B

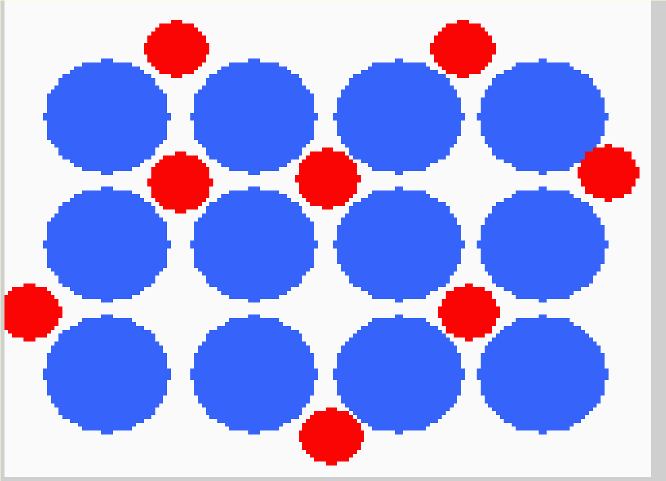
Examples:
(Cu,Ni)
(Au,Ag)
(Cu,Pt)
(Cu,Pd)



● interstitial solid solution

Interstitial phases predominant in steels and ferrous-based alloys, where elements such as C and N occupy the interstitial sites of the ferrite and austenite lattices

Example: (Fe,Cr):(C,Va)
More general: (Fe,Cr,Ni,Mn…)$_u$:(Va,C,N,…)$_v$



Conversions and constants

- Avogadro's number: N=6.022 × 1023 mol^{-1}
- Boltzmann's constant: k=1,3806 J/K
- Gaz constant: R=8.314 J/K mol = 1.987 cal/K mol
- G(cal) = G(J) / 4.184
- T(K) = T(°C) + 273.15
- 1 inche = 2,5 cm
- 1 cm = 0,4 inche