Phase Diagrams

Experimental Information and Thermodynamic Evaluation

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Outline

1. Applications of thermodynamic description of multicomponent systems for materials and processing development

2. Acquisition of reliable data

3. Calculation of phase diagrams

4. Thermodynamic databases

Outline

1 Applications of thermodynamic description of multicomponent systems for materials and processing development

- Example

- Typical information needed by users for practical applications

- Different ways to represent diagrams

2 Acquisition of reliable data

3 Calculation of phase diagrams

4 Thermodynamic databases

Example
Microstructural design of aluminium alloys

- ▶ **Information directly usable by casting plants:**

  - ✦ Liquidus temperature of an alloy ➔ adjustment of the casting temperature.
  - ✦ Location of eutectic valleys ➔ limits of the field of primary precipitates, coarse and detrimental to a good workability.
  - ✦ Definition of composition and temperature fields allowing a complete dissolution of specific precipitates ➔ optimization of homogenization treatment.

- ▶ **Industrial aluminium alloys:**

  - ✦ Major alloying elements (Cu, Mg, Zn, Si, Mn).
  - ✦ Minor alloying elements (Mn, Cr, Zr, Ti).
  - ✦ Impurities (Fe, Si).

➔ Need of thermodynamic calculations associated with a suitable database.

Typical information needed by users for practical applications

- **Evaluation of thermodynamic properties:**
    - Heat capacity
    - Gibbs energy of formation
    - Partial pressures
    - Chemical potentials, activity...

- **Compositions for phases in equilibrium, phase fraction.**

- **Isothermal and isopleth sections.**

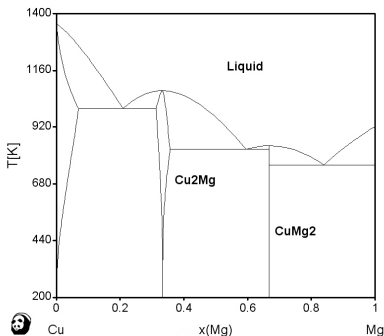- **Solidification paths, fraction of phases during solidification ...**

$\Rightarrow$ **Thermodynamic description of multicomponent systems:** maps for materials and processing development
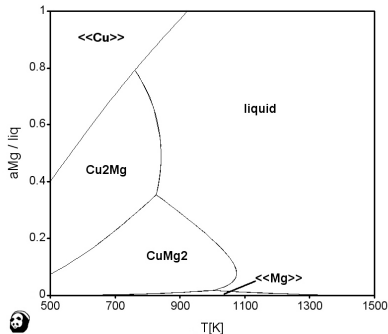
Different ways to represent diagrams (I)

To obtain an optimum representation of thermodynamic data of multicomponent systems, several types of *2D* diagrams can be considered:

✦ **Phase diagrams:** Regions with different sets of stable phases separated by lines (*"zero phase fraction" line*). Give the phase stability domains.
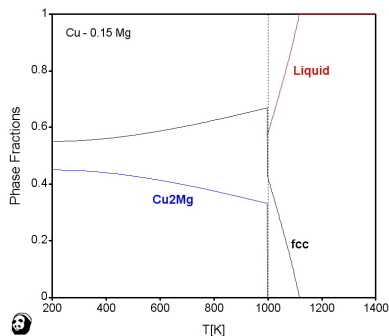
→ T (or P) *vs* composition plots
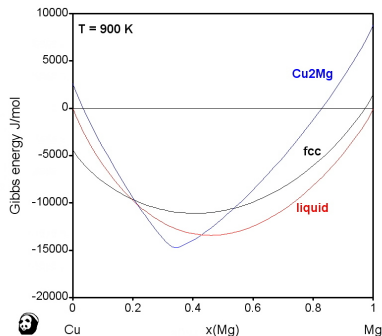
→ T *vs* chemical potential plots

Different ways to represent diagrams (II)

✦ **Property diagrams:** How the system varies with one independent variable.
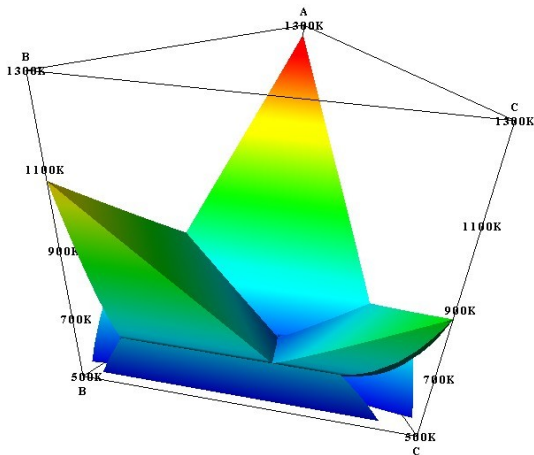
→ Phase fraction *vs* temperature plots

→ Gibbs energy *vs* composition plots

Different ways to represent diagrams (III)

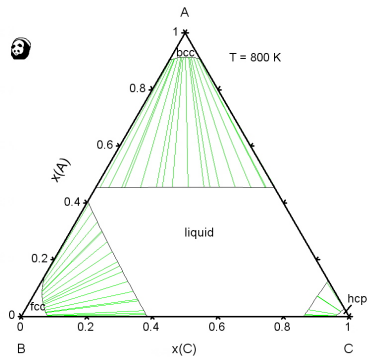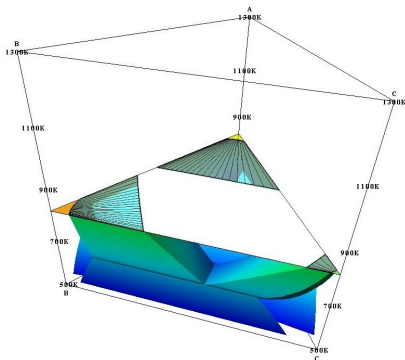✦ **Ternary phase diagrams**

➔ Space model

Different ways to represent diagrams (IV)
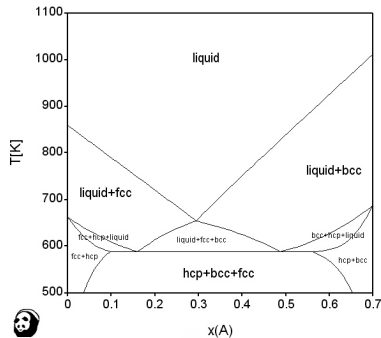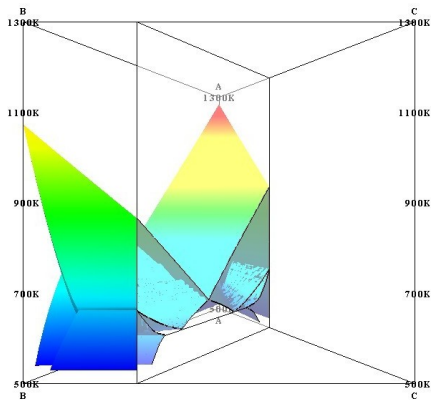
✦ **Ternary phase diagrams**

→ Isothermal sections

Different ways to represent diagrams (V)

✦ **Ternary phase diagrams**

➜ Vertical sections

Different ways to represent diagrams (VI)

✦ **Ternary phase diagrams**

→ Liquidus projection

Outline

1 Applications of thermodynamic description of multicomponent systems for materials and processing development

2 Acquisition of reliable data

- Various methods of determination of experimental data

- Reliability of experimental data

- Experimental investigations and thermodynamic evaluation: Two complementary approaches

3 Calculation of phase diagrams

4 Thermodynamic databases

Various methods of determination of experimental data (I)

- **Phase diagram data:**
  ➥ **Static method: isothermal treatments on equilibrated alloys or diffusion couples.**

  - ✦ Phase compositions ➔ tie-lines, tie-triangles (SEM-EDX, EPMA)
  - ✦ Structural properties of phases (XRD, TEM)

- **Phase diagram data:**
  ➥ **Dynamic method: heating/cooling experiments (DTA/DSC...)**

  - ✦ Liquidus, solidus temperatures
  - ✦ Invariant temperatures
  - ✦ Solidification paths

Fe–Ti phase diagram

N. Dupin, Constitution de bases de données de type Calphad, formation continue 2008.

Various methods of determination of experimental data (II)

▶ **Thermochemical quantities:** (calorimetry, mass spectrometry...)

Fe–Ti system. Activity in the liquid phase

Fe–Ti system. Heat capacity of Fe2Ti phase

N. Dupin, Constitution de bases de données de type Calphad, formation continue 2008.

Various methods of determination of experimental data (III)

▶ **Thermochemical quantities:** (calorimetry, mass spectrometry...)

Fe–Ti system. Mixing enthalpy in the liquid phase

Fe–Ti system. Chemical potentials in the liquid phase

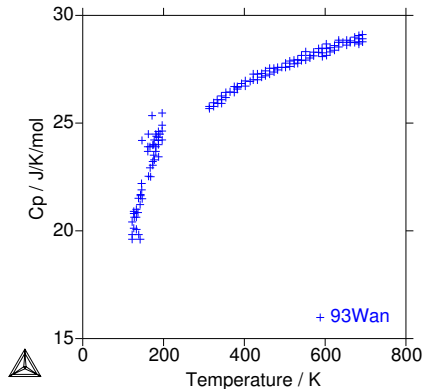*N. Dupin, Constitution de bases de données de type Calphad, formation continue 2008.*

Various methods of determination of experimental data (IV)

▶ **Crystal structure identification:**
  ➡ XRD, ND

    ◆ Structural properties of phases
    ◆ Number and site occupation
    ◆ Magnetic transitions

▶ **Ab-initio methods**, quantum mechanical (DFT) calculations:

    ◆ Heat of formation for intermetallic compounds (at 0 K)
    ◆ Estimation of specific heat

Reliability of experimental data

→ Criteria for generating reliable data (*J.F.Smith, Mater. Sci. Eng., 48 (1981) 1*):

1. **Use of an experimental technique with suitable resolution.**

   ◆ Analyze of fine-grained structure.

2. **Establishment and retention of equilibrium for the regime of interest.**

   ◆ "High temperature data are more likely to represent equilibrium, even though of lesser precision, than lower temperature data".

3. **Suitable characterization of materials to ensure that the determination of equilibria is representative of the system of interest.**
   To be avoided:

   ◆ Impurities, contaminating environment (minor amount of oxygen or hydrogen...).
   ◆ Inhomogeneous samples.
   ◆ Deviation from the nominal composition (Oxidization, melting loss...)

Experimental data and thermodynamic evaluation: two complementary approaches

→ Application of physical chemistry principles to the calculation of equilibria in multicomponent systems

These thermodynamic evaluations can be used:

- ▶ To check the reliability of experimental data and to study the consistency between the data.

- ▶ To validate experimental methods.

- ▶ To define experiments to be carried out.

- ▶ To point out necessary additional experiments.

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1. Applications of thermodynamic description of multicomponent systems for materials and processing development

2. Acquisition of reliable data

3. Calculation of phase diagrams

   - Computational thermodynamics and Calphad method

   - Principle of phase equilibria

   - Phase diagrams calculations

   - From binary to multicomponent systems

4. Thermodynamic databases

Computational thermodynamics

- Ab-initio / Monte Carlo / Molecular Dynamics

    + Exact

      Predictive

    − Long computation time

      Limited applications

- Calphad method

    + Multicomponent systems

      Fast calculations

    − Non-predictive

      Parameters without physical meaning

Calphad method to perform a system's assessment

Determination of the Gibbs functions G=f(T,P,x) ⬅

Calculation of equilibrium diagrams and any thermodynamic quantity ⬅

Théorie
Calculs ab-initio ↔ Estimations ↔ Expériences

Modèles

Ajustement des paramètres

Grandeurs thermodynamiques

Stockage en banque de données

Equilibre

Représentation graphique

Applications

d'après http://www.thermocalc.se

Principle of phase equilibria
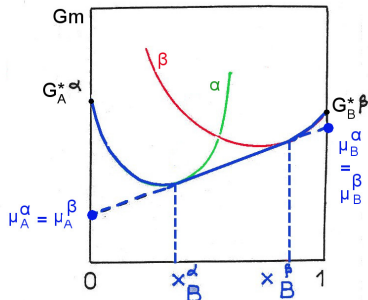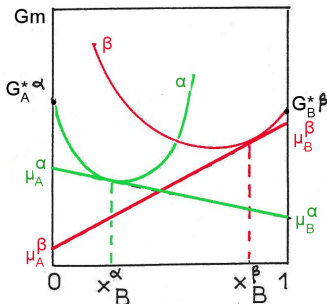
In a closed system at constant T and P, equilibrium between phases (from 1 to ϕ) requires that they have the same value for the chemical potential of each component.

$$\mu_i^1 = \mu_i^2 = ... = \mu_i^\alpha = ... = \mu_i^\phi \qquad \textbf{for i from 1 to c}$$

In a binary system:

$$\mu_A^\alpha(x_B^\alpha, T, P) = \mu_A^\beta(x_B^\beta, T, P) \qquad \mu_B^\alpha(x_B^\alpha, T, P) = \mu_B^\beta(x_B^\beta, T, P)$$

Common tangent construction: The composition of the points of tangency gives the composition of two phases in equilibrium at given T and P.

Phase equilibria in a multicomponent system

→ Minimization of Gibbs free energy of the system.

ou → Resolution of a set of equation giving the same value for the chemical potential of each component in the different phases.

Gibbs energy function formulation:

$$G = \sum_{j=1}^{\phi} n^j \ G^j \qquad \text{with} \qquad n_i = \sum_{j=1}^{\phi} n_i^j$$

- G^j: **Gibbs energy function for j phase**
- n_i^j: **number of moles of species j in the i phase**

$G^\phi = f(T, P, x, T_c, \beta)$

Phase diagrams calculations (I)
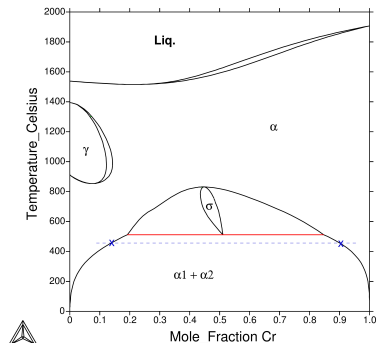
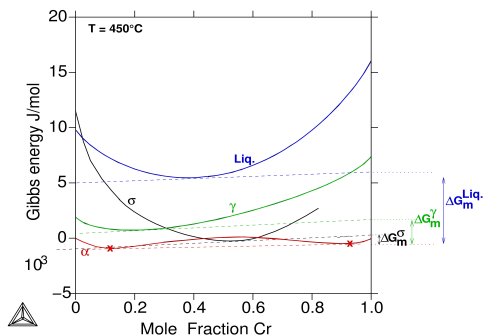Requirements:

- Database with the description of Gibbs energy functions for each phase

- Minimization software with optimization routines for model parameters
  - Derivation (Lagrange multiplier)
  - Direct numerical minimization (Monte-Carlo)

Phase diagrams calculations (II)

Evolution of driving force for each phase as a function of tempetaure and composition
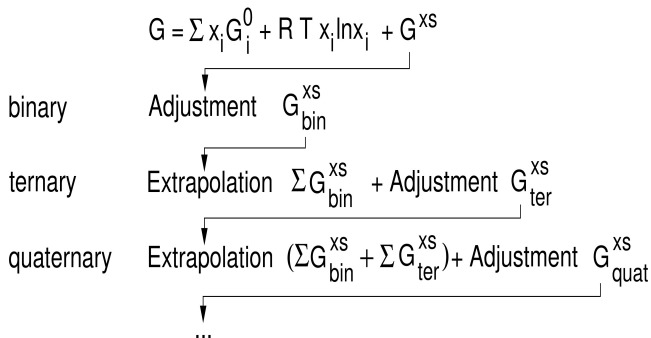→ evaluation of phase boundaries.

From binary to multicomponent systems (I)

General expression of the Gibbs energy for all solution phases ϕ :

$$G(\phi, T) = G_{ref}(\phi, T) + \Delta_{mix} G^{id} + \Delta_{mix} G^{xs} + \Delta_{mix} G^{magn}$$

- G_{ref} : **Gibbs energy reference state, contribution of the pure components of the phase to the Gibbs energy** : $G_{ref}(\phi, T) = \sum_i x_i \, G_i^0(\phi, T)$

- $\Delta_{mix} G^{id}$: **Ideal mixing contribution**

- $\Delta_{mix} G^{xs}$: **Gibbs excess energy of mixing, contribution due to non-ideal interactions between the components**

- $\Delta_{mix} G^{magn}$: magnetic Gibbs energy contributions

From binary to multicomponent systems (II)

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

binary   Adjustment G_{bin}^{xs}

ternary   Extrapolation $\sum G_{bin}^{xs}$ + Adjustment G_{ter}^{xs}

quaternary   Extrapolation $(\sum G_{bin}^{xs} + \sum G_{ter}^{xs})$+ Adjustment G_{quat}^{xs}

     ...

U. Kattner, JOM, 14-19, (1997)

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   - Gibbs energy function formulation

   - Calculations of solid-liquid equilibria, case of regular solution theory

   - A corresponding simple database

   - Some example cases

Gibbs energy function formulation (I)

General formula of the molar Gibbs energy for all solution phases ϕ :

$$G(\phi, T) = G_{ref}(\phi, T) + \Delta_{mix}G^{id} + \Delta_{mix}G^{xs} + \Delta_{mix}G^{magn}$$

- **Gibbs energy reference state** : $G_{ref}(\phi, T) = \sum_i x_i \, G_i^0(\phi, T)$

Generally reference state SER: Enthalpy of pure components in their most stable form Φ under P^0 and 298.15 K

$$GH_i^{SER} = G_i^0(\psi, T) - H_i^{0,SER}(\psi, 298.15)$$

$$G_i^0(\phi, T) - H_i^{0,SER}(\psi, 298.15) = \underbrace{G_i^0(\phi, T) - G_i^0(\psi, T)}_{lattice\ stability} + GH_i^{SER}$$

A.T. Dinsdale, Calphad, 15(4), (1991), 317.

Gibbs energy function formulation (II)

Thermodynamic model:

$$GH_i^{SER} = a + b\ T + c\ T \ln T + \sum_k d_k\, T^k \qquad \text{with } k = 2, 3, -1$$

$$\Rightarrow S_i^{\phi}(T) = -\left(\frac{\partial G}{\partial T}\right)_P = -b - c - c\ \ln T - \sum_k k\, d_k\, T^{k-1}$$

$$\Rightarrow H_i(\phi, T) - H_i^{SER}(\psi, 298.15) = a - c\ T - \sum_k (k-1)\, d_k\, T^k$$

$$\Rightarrow C_p = -\left(\frac{\partial H}{\partial T}\right)_P = -c - \sum_k k\, (k-1)\, d_k\, T^{k-1}$$

a, b, c, d_k Adjustable parameters <u>without</u> physical meaning.

Gibbs energy function formulation (III)

- **Gibbs excess energy of mixing** $\Delta_{mix} G^{xs}$

Binary and ternary interactions: $\Delta_{mix} G^{xs} = \sum\limits_{i,j} G_{ij}^{xs} + G_{ijk}^{xs}$
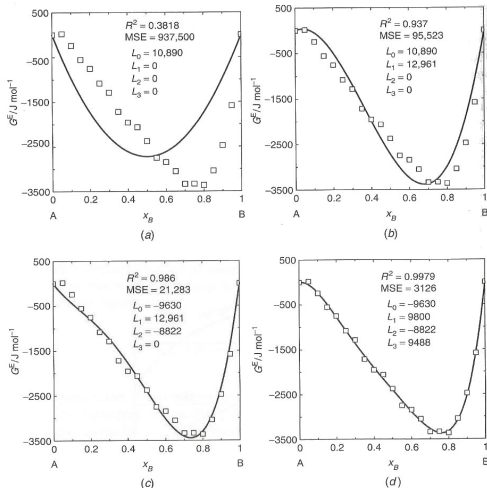
$\Rightarrow G_{ij}^{xs} = x_i \, x_j \sum\limits_{\nu=0}^{k} L_{ij,\nu} \, (x_i - x_j)^\nu$ Redlich-Kister equation

$\Rightarrow G_{ijk}^{xs} = x_i \, x_j \, x_k \, (x_i \, L_i + x_j \, L_j + x_k \, L_k)$

Gibbs energy function formulation (IV)

For a binary system:

$$\Delta_{mix}G^{xs} = x_A\, x_B \sum_{\nu=0}^{k} L_\nu\, (x_A - x_B)^\nu = L_0 x_A x_B + L_1(x_A - x_B) + L_2(x_A - x_B)^2 + ...$$

Y.A. Chang, W.A. Oates, Materials Thermodynamics, J. Willey&Sons, 2010.

Calculations of solid-liquid equilibria
Using regular solution theory for binary systems

Relationships between topological features and interactions for binary systems

- Gibbs energy for a regular solution

$$G^{\phi}(T) = x_A G^0(A, T) + x_B G^0(B, T) + \lambda x_A x_B + RT[x_A \ln x_A + x_B \ln x_B]$$

- Gibbs energy of a liquid L and a solid solution α, reference pure liquids.

$$G(L, T) = \lambda_L x_A x_B + RT[x_A \ln x_A + x_B \ln x_B]$$
$$G(\alpha, T) = \lambda_\alpha x_A x_B + RT[x_A \ln x_A + x_B \ln x_B] - x_A \Delta_{fus} G(A, T) - x_B \Delta_{fus} G(B, T)$$
$$\text{with } \Delta_{fus} G(i, T) = \Delta_{fus} S(i)(T_{fus}^i - T)$$

- The topological features depend on :
  - the solution behaviour of solid and liquid phases
  - the melting temperatures of pure components
  - the melting entropies of pure components

```
$ A-B SYSTEM

ELEMENT /-    ELECTRON_GAS      0             0            0 !
ELEMENT VA    VACUUM            0             0            0!
ELEMENT A     FCC_A1            2.6982E+01    4.5773E+03   2.8322E+01!
ELEMENT B     FCC_A1            6.3546E+01    5.0041E+03   3.3150E+01!


PHASE liquid  %  1 1 !
CONSTITUENT liquid : A,B : !
PARAMETER G(liquid,A;0)  298.15 0;   6000  N !        Reference state :
PARAMETER G(liquid,B;0)  298.15 0;   6000  N !        A and B pure liquids


PHASE FCC_A1  %  1 1 !
CONSTITUENT FCC_A1 : A,B : !
PARAMETER G(FCC_A1,A;0)  298.15  -11730 + 10*T;  6000  N !     - ΔGfus(i)
PARAMETER G(FCC_A1,B;0)  298.15  -6730 + 10*T;   6000  N !     = ΔSfus(i) [ T - Tfus(i) ]

$L0 for liquid
PARAMETER G(liquid,A,B;0)  298.15  20000;  6000  N !   λL

$L0 for FCC_A1
PARAMETER G(FCC_A1,A,B;0)  298.15  20000;  6000  N !   λS
```
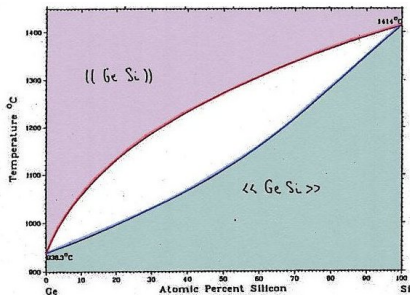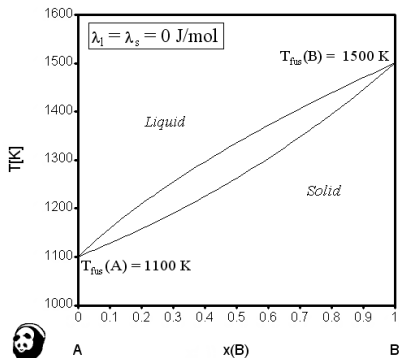
Example 1
Complete Miscibility in Liquid and Solid States

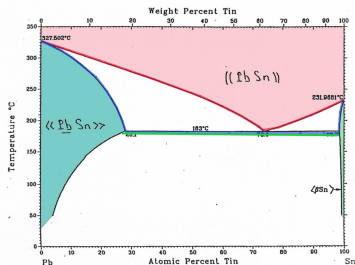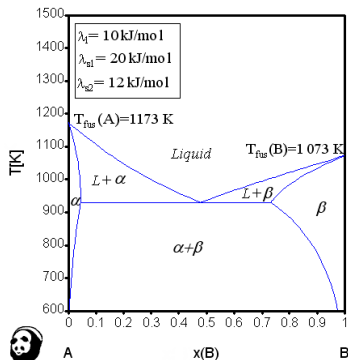- ▶ Ideal solution behaviour for the solid and liquid phases ⇒ cigar-shaped phase diagram

$$\Delta S_{fus}^A = 20 \quad \Delta S_{fus}^B = 20 \quad [J.mol^{-1}.K^{-1}]$$

Example 2
Complete Miscibility in the Liquid State and limited Miscibility in the Solid State

▶ Strong repulsive interactions

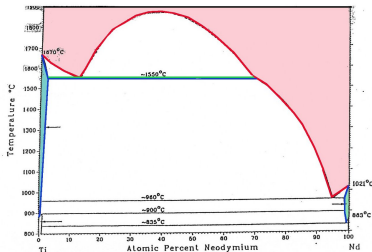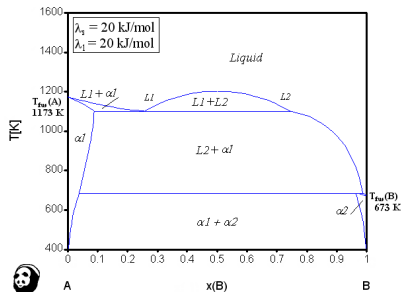 • Binary EUTECTIC phase diagram, pure A and B purs with different structures

$\Delta S_{fus}^A = \Delta S_{fus}^B = 10 \quad [J.mol^{-1}.K^{-1}]$
$\Delta H(\alpha - \beta)^A = 5000 \quad [J.mol^{-1}] \quad \Delta H(\beta - \alpha)^A = 3000 \quad [J.mol^{-1}]$

Example 3
Complete Miscibility in the Liquid State and limited Miscibility in the Solid State

- ▶ Strong repulsive interactions
- ▶ Relatively low melting points
    - **MONOTECTIC reaction :** $l1_M \rightleftharpoons l2_N + \alpha_A$

$$\Delta S_{fus}^A = \Delta S_{fus}^B = 20 \quad [J.mol^{-1}.K^{-1}]$$

Conclusions

Strong link between

Experimental Information and **Thermodynamic Evaluation**

a powerful way of knowledge of materials

✦ References

* H.L. Lukas, Computational Thermodynamics, Cambridge UP, 2007.

* M. Hillert, Phase equilibria, phase diagrams, phase transformations, Cambridge UP, 1998.

* J.C. Zhao, Methods for phase diagram determination, Elsevier, 2007.

* Topological Features of Binary Phase Diagrams:
http://www.tms.org/journals/JOM/0312/Chang/Chang-0312.html