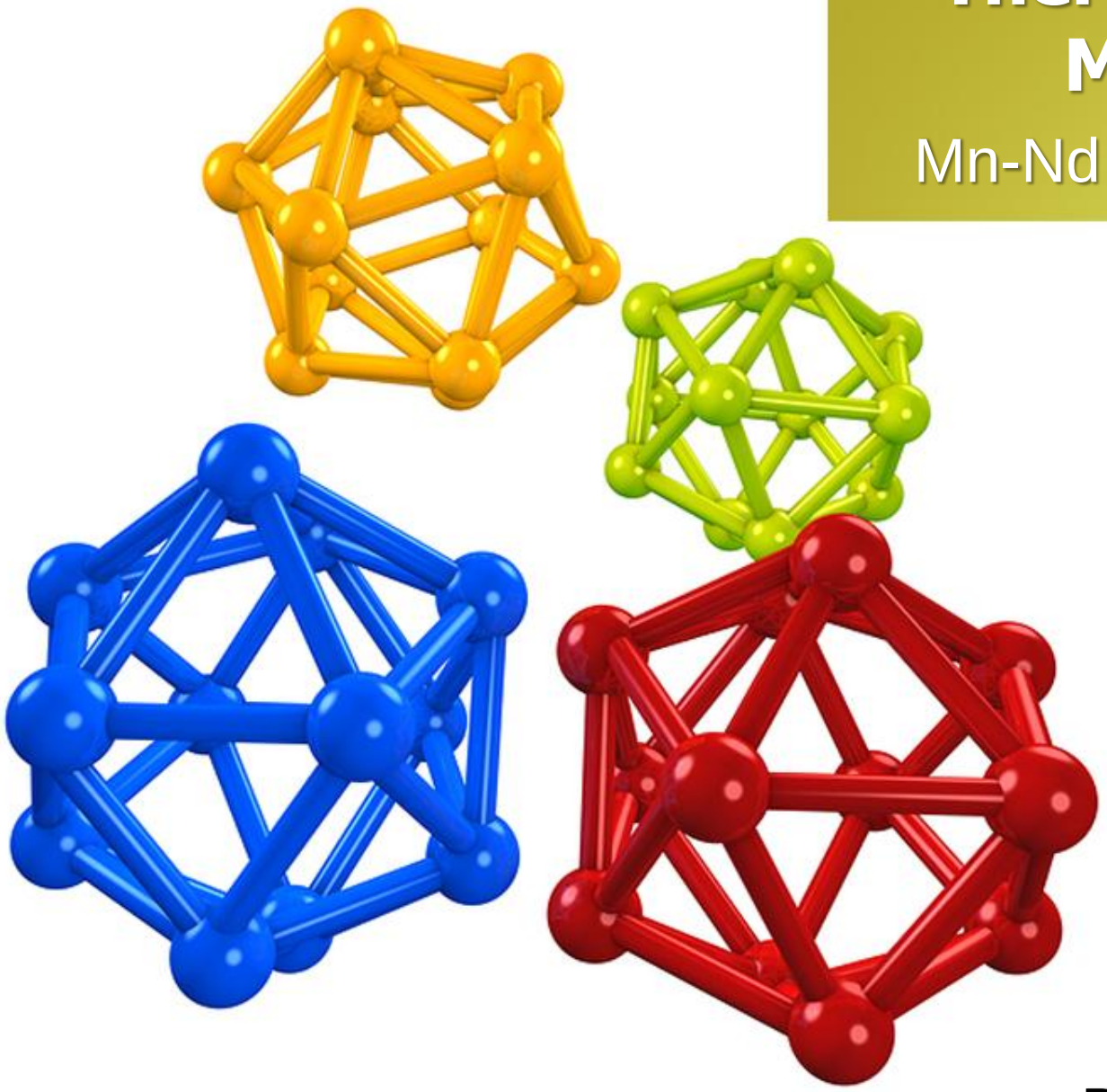
Thermodynamic Modeling

Mn-Nd phase diagram



By

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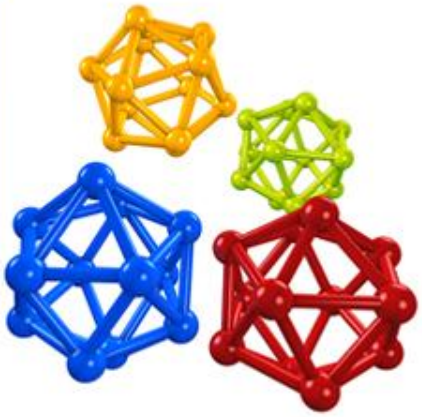
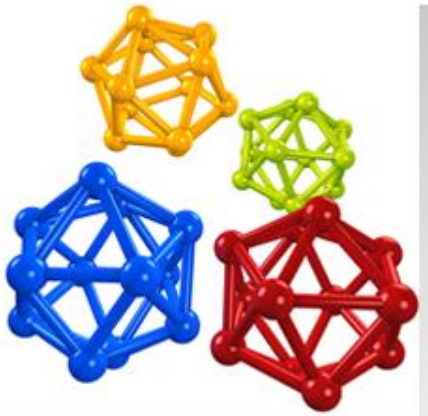
Presented to

Dr. Mamoun Medraj

Outlines

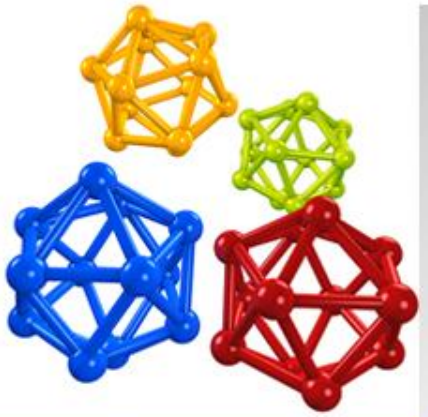


- Introduction
- Experimental data
- Gibbs energy models
- Thermodynamic modeling and experimental investigation of Mn-Nd phase diagram
- Conclusions



Introduction

- Phase diagram can be calculated from Gibbs energy function of phases.
- The required Gibbs energy functions are usually obtained by a computer-assisted statistical procedure, using experimental thermochemical and constitutional data as input.
- CALPHAD (CALculation of PHAse Diagram).



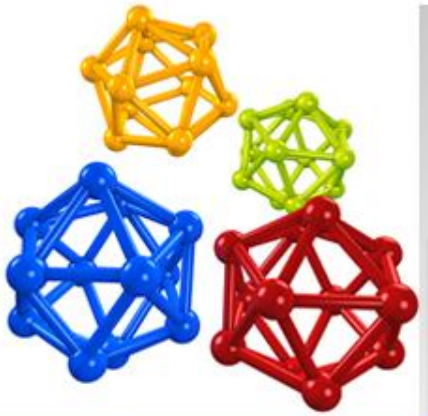
Experimental Data

❖ **Steps of thermodynamic optimization of a phase diagram:**

First step

- Collecting and categorizing any experimental information linked to Gibbs energy.

  ✓ Thermochemical data
  ✓ Crystallographic data
  ✓ Review articles



Experimental Data

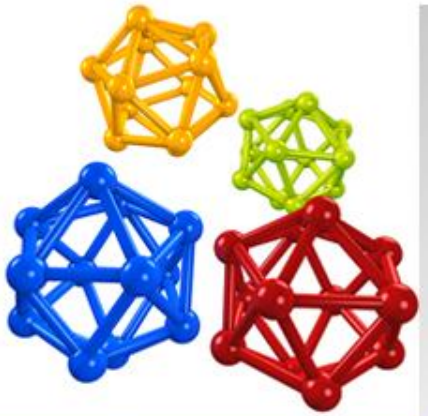
Second step

- The critical evaluation of the collected data by discarding the bad or contradictory data, using the following methods:

Recording the data

- ✓ The used technique
- ✓ Phases presented
- ✓ Purity of the samples
- ✓ Experimental conditions
- ✓ Quality and accuracy of the measurements

Graphical comparison



Experimental Data

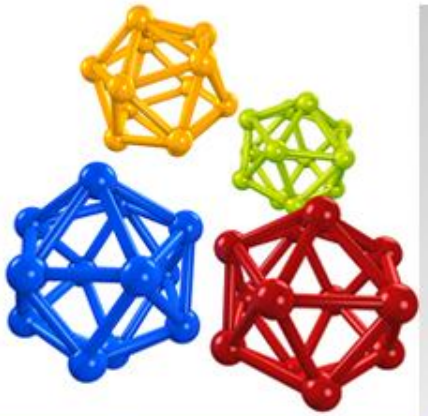
- The main difficulty in the phase diagram modeling is that the start values must be supplied for all model parameters.

❖ **If the initial experimental information are available, then:**

i. It is more practical to begin optimization with minimal data set

Example:

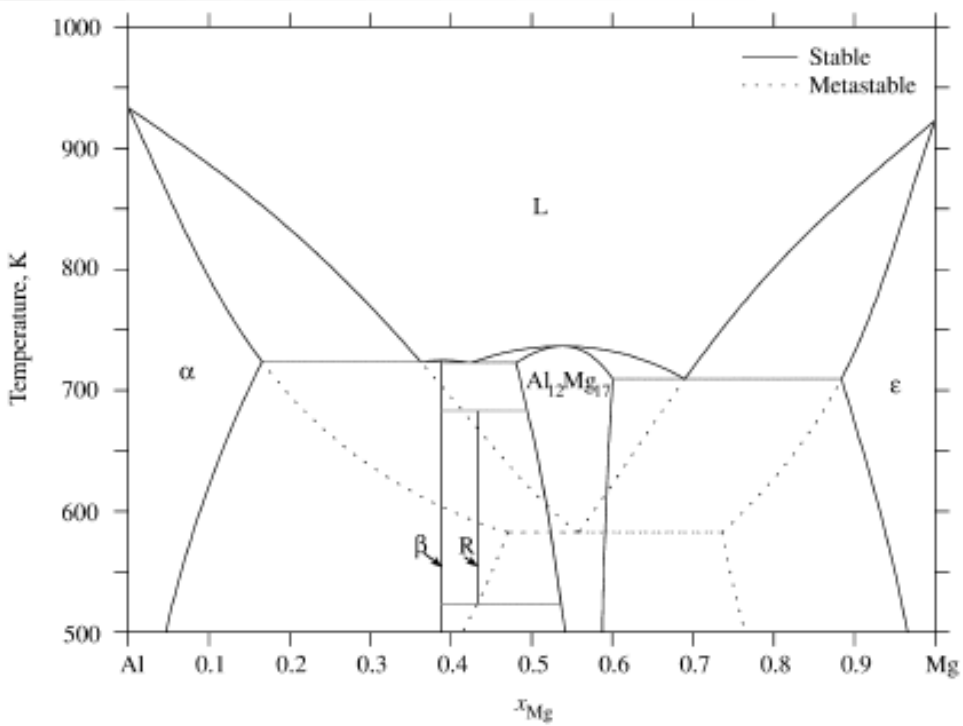
- ❑ For binary systems, it is enough to start with data pertaining to:
- ✓ Invariant points
- ✓ Congruent melting
- ❑ For ternary systems, the start begins with extrapolating the data from the constituent binaries.



Experimental Data

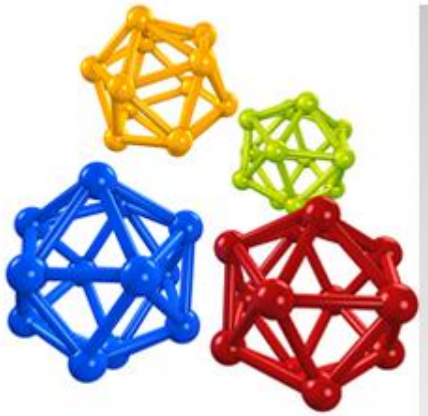
ii. The experimental data can also be extrapolated from the metastable equilibrium PD

- This can reduce the number of phases that may optimized together



Stable and metastable phases of Al-Mg phase diagram

H. Kumar, and P. Wollants, 2001



Experimental Data

- Once the initial description is obtained by the minimal data set, more experimental data can be added.

❖ **More experimental data can be obtained by:**

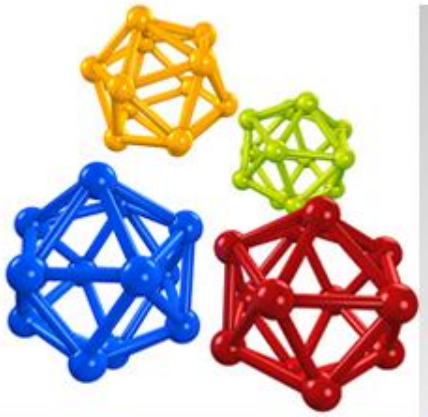
i. Estimation of the experimental data using different methods

Example:

- ❑ $\Delta H_{formation}$ of transition metal compounds can be obtained by *Miedema`s method*
- ❑ $Cp_{(Molar)}$ can be approximated by *Kopp-Neumann rule*
- ❑ Excess partial molar Gibbs energies can be calculated by

$$^{xs}G_A = RT \ln \gamma_A \text{ and } ^{xs}G_B = RT \ln \gamma_B$$

- ❑ Experimental slopes of the phase boundaries involving the terminal phases in binary systems can be checked by *Van't Hoff`s equation*



Experimental Data

- Application of Van't Hoff`s equation

$$(dX/dT)_{solidus}-(dX/dT)_{liquidus}=\Delta H_{fus}/RT_m^2$$

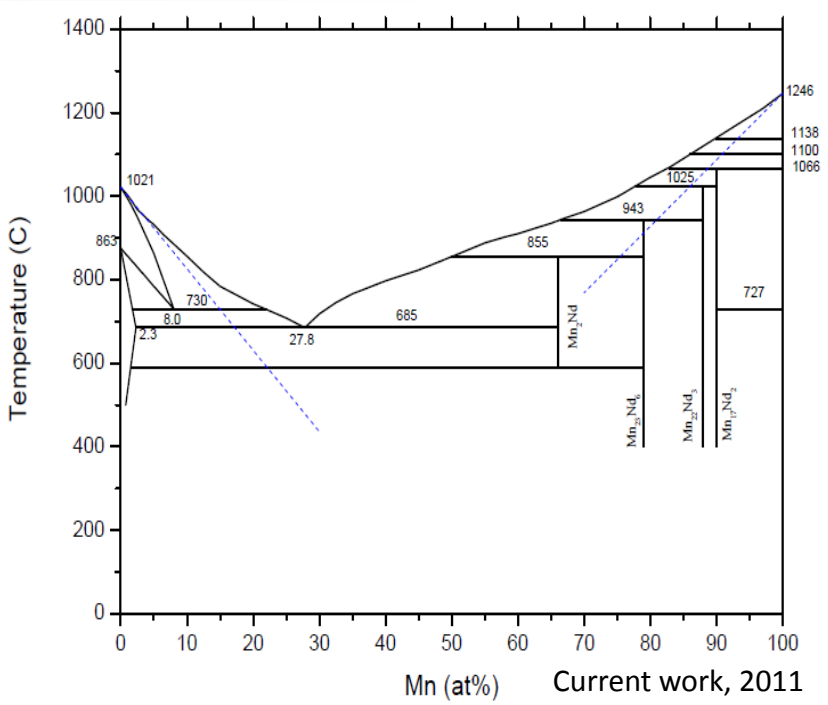
X: is the mole fraction of the solute

ΔH_{fus}: Enthalpy of fusion

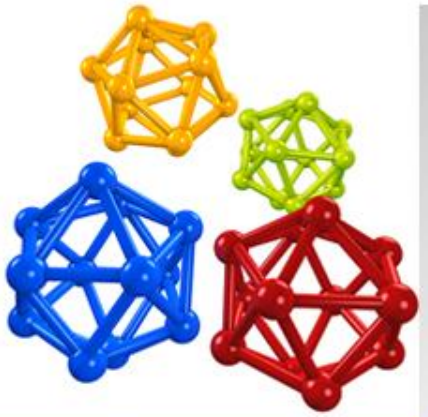
T_m: melting point of the pure element

The initial value of $(dX/dT)_{solidus}$ for the terminal phases=0, then:

$$\Delta H_{fus(Nd)}=-(dX/dT)_{liq(Nd)}\times RT_m^2$$

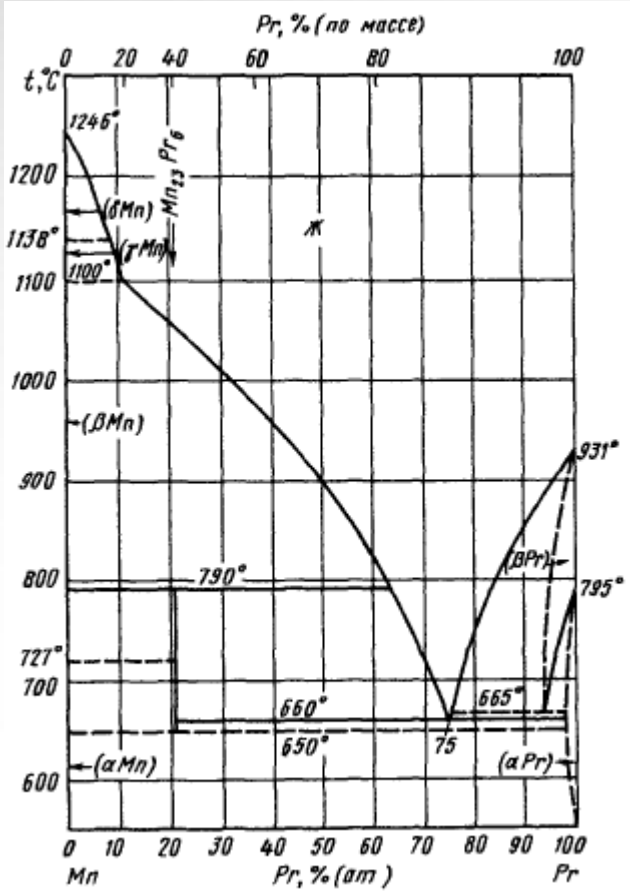


Current work, 2011



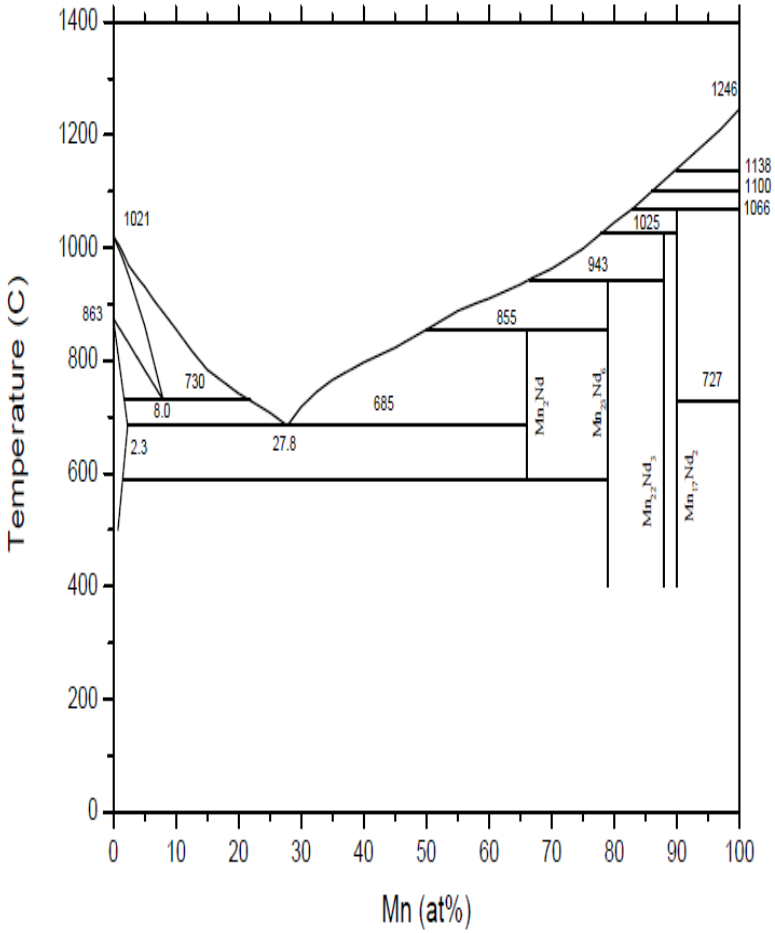
Experimental Data

ii. Data of similar systems can also offer a great deal of information

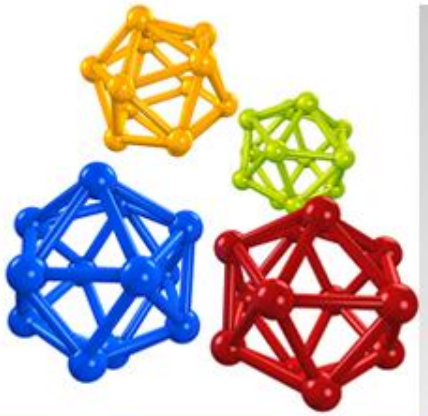


Mn-Pr phase diagram from literature

Saccone et al., 1985



Mn-Nd phase diagram recently studied



Gibbs energy models

$$G = G^{ref} + G^{ideal} + G^{xs} + G^{phys}$$

G^{ref}: Reference surface for Gibbs energy

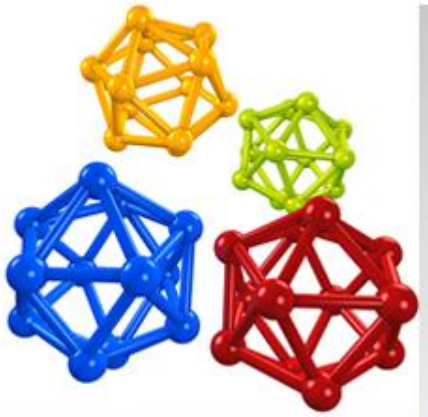
G^{ideal}: Gibbs energy for ideal mixing

G^{xs}: is the excess Gibbs free energy

G^{phys}: physical contribution energy

❖ Types of thermodynamic models:

- ❑ Regular Solutions Models
- ❑ Sublattice Model
- ❑ Associated Solutions
- ❑ Cluster Variation Model
- ❑ Quasi-chemical Model
- ❑ Cluster Expansion Model



Gibbs energy models

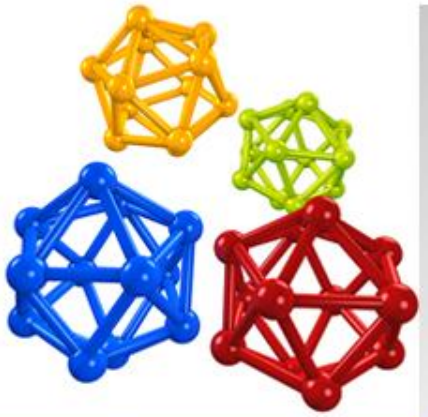
- Choice of Gibbs energy model for a phase should be physically adequate for the P-X-T domain, in which the phase is stable.

- The model should have extrapolating capability in the higher-order systems.

- The good strategy to start the optimization process with simple Gibbs free energy models which have few model parameters.

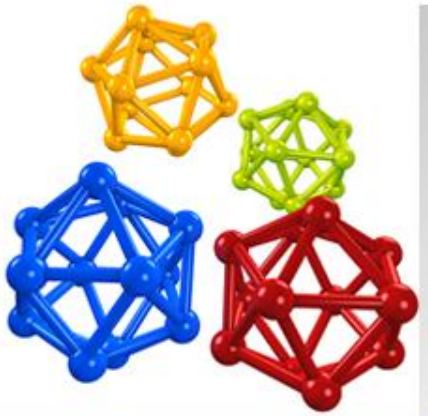
Example:

✓ As a first approximation, all intermediate phases in a binary system can be treated as stoichiometric compounds.



Mn-Nd Phase diagram

- The Mn-Nd phase diagram is reconstructed experimentally using ICP, DSC, SEM/EPMA, XRD and microscopic analysis.
- No thermodynamic description was carried out on this system.
- The thermodynamic data of the system are obtained from similar systems as mentioned in the literature
- In this work, the liquid solution phases will be modeled with the quasi-chemical model (QCM).
- Random solution model is used for terminal solid solutions.



Mn-Nd Phase diagram

- The Gibbs energy for the terminal solid solution phases is described by the following equation

$$G^{\phi} = x_i {}^{0}G_i^{\phi} + x_i {}^{0}G_j^{\phi} + RT[x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^{\phi}$$

Ø: is the phase of interest

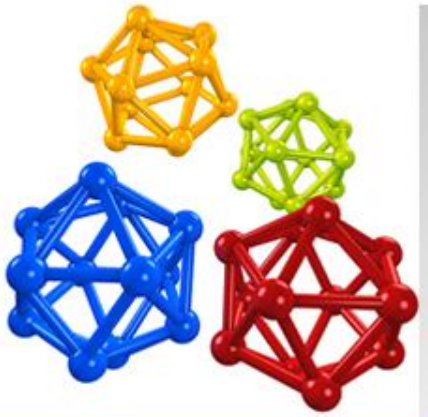
X_i and X_j: are the mole fractions of components *i* and *j* respectively

- The excess Gibbs energy is described by the *Redlich-Kister* polynomial model

$${}^{ex}G^{\phi} = x_i . x_j \sum_{n=0}^{n=m} {}^{n}L_{i,j}^{\phi} (x_i - x_j)^n$$

$${}^{n}L_{i,j}^{\phi} = a_n + b_n \times T$$

- Where, a and b: are the parameters of the model need to be optimized.

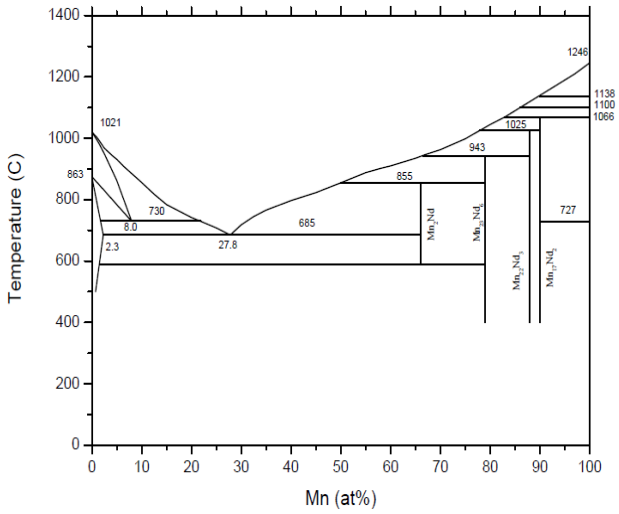


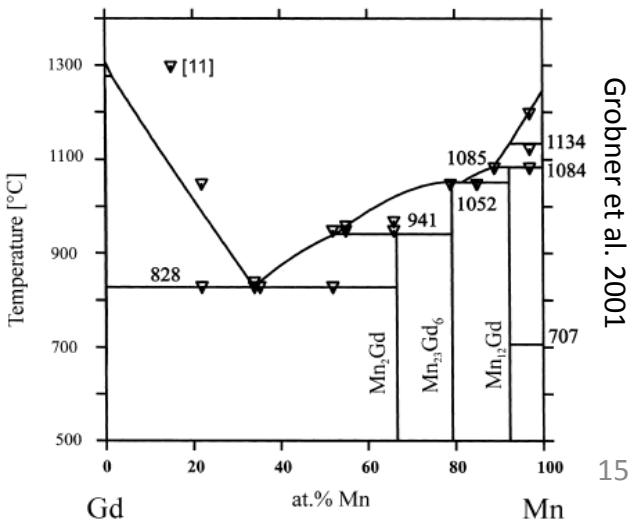
Mn-Nd Phase diagram

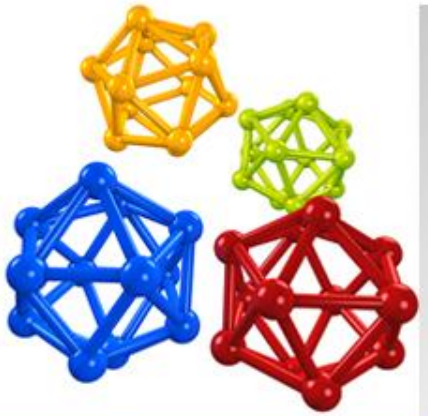
❖ Why quasi-chemical model?

- ✓ It offers greater flexibility in optimizing the parameters for the systems show large degree of SRO in the liquid.
- ✓ It is more realistic because it considers the preferential formation of the nearest neighbor A-B pairs for SRO.
- ✓ Choosing the QCM for liquid phase leads to the consistency with the other existing databases developed with the same model.

- Similarity between Mn-Gd system and Mn-Nd system is found, as shown.







Mn-Nd Phase diagram

- From similarity with Mn-Gd system, the parameters ($Jmol^{-1}$) can be concluded :

L(LIQUID,Gd,Mn;0)= -5020.871+0.56166*T

L(LIQUID,Gd,Mn;1)= 1041.42

G($Mn_{12}Gd$,Mn:Gd;0)= -52000+12.1*T+12*G_{Mn}+G_{Gd}

G($Mn_{23}Gd_6$,Mn:Gd;0)= -185000+27.6*T+23*G_{Mn}+6*G_{Gd}

G(Mn_2Gd,Mn:Gd;0)= -19242+2.87*T+2*G_{Mn}+G_{Gd}

G(FCC A1,Gd;0)= 10000+G_{Gd}

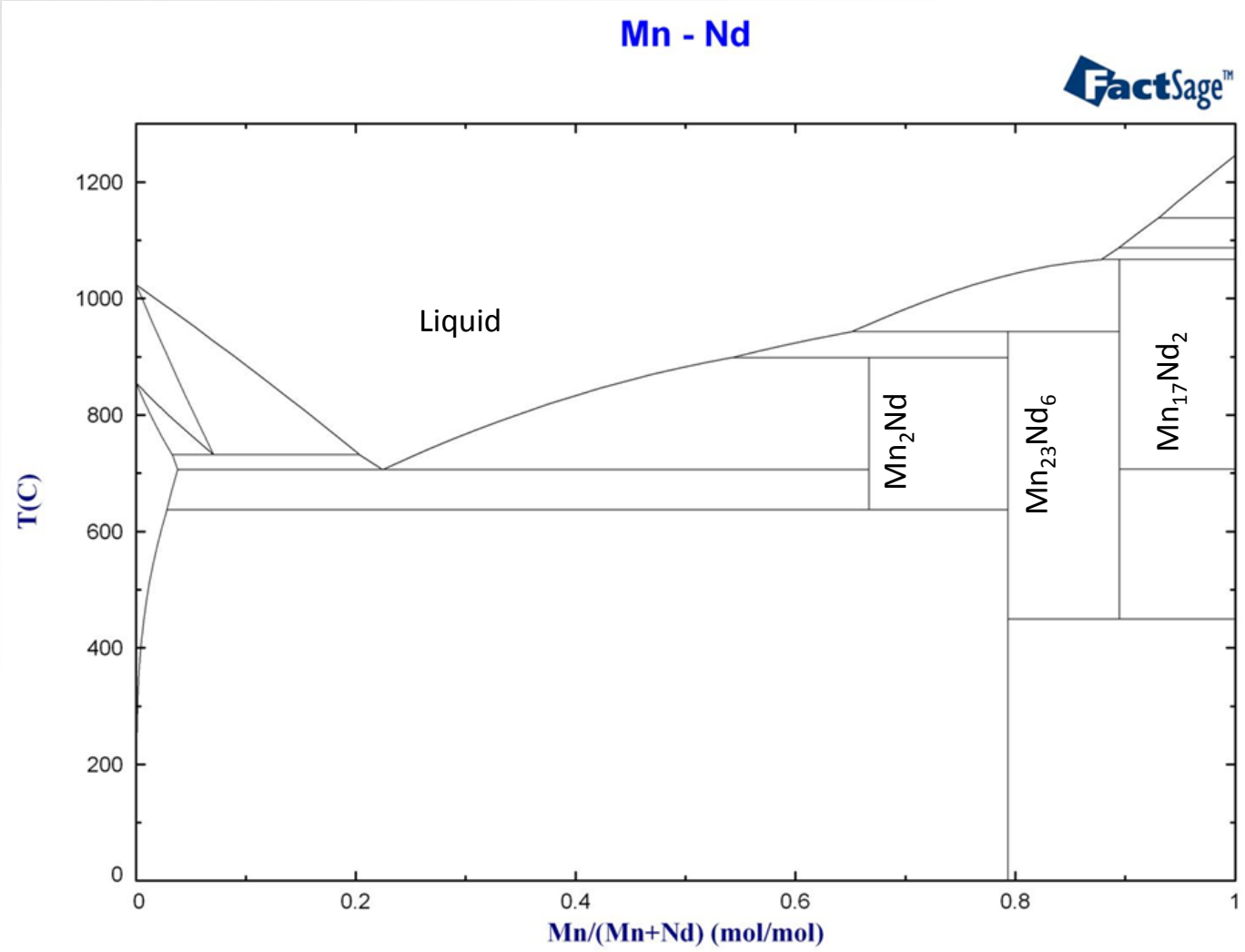
L(BCC A2,Gd,Mn;0)= 50000

L(HCP A3,Gd,Mn;0)= 50000

L(FCC A1,Gd,Mn;0)= 50000

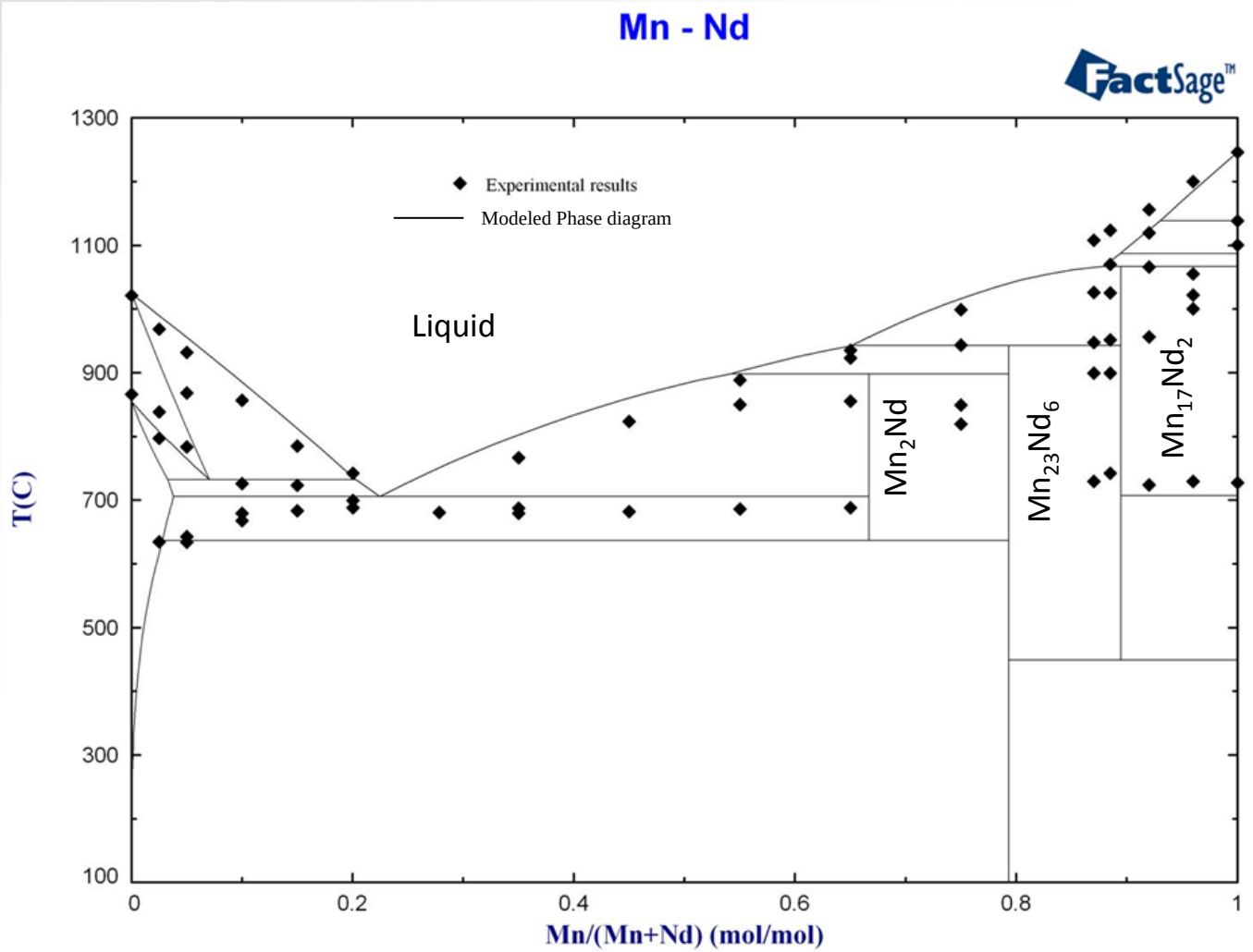
Mn-Nd Phase diagram

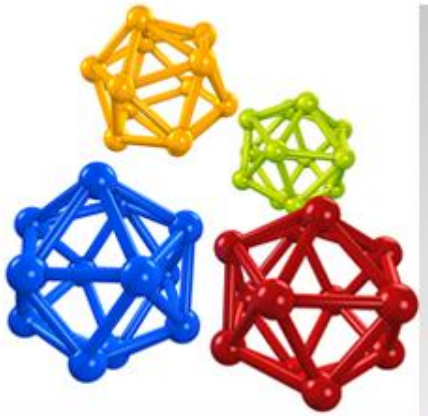
- Applying the obtained parameters for Mn-Nd phase diagram optimization:



Mn-Nd Phase diagram

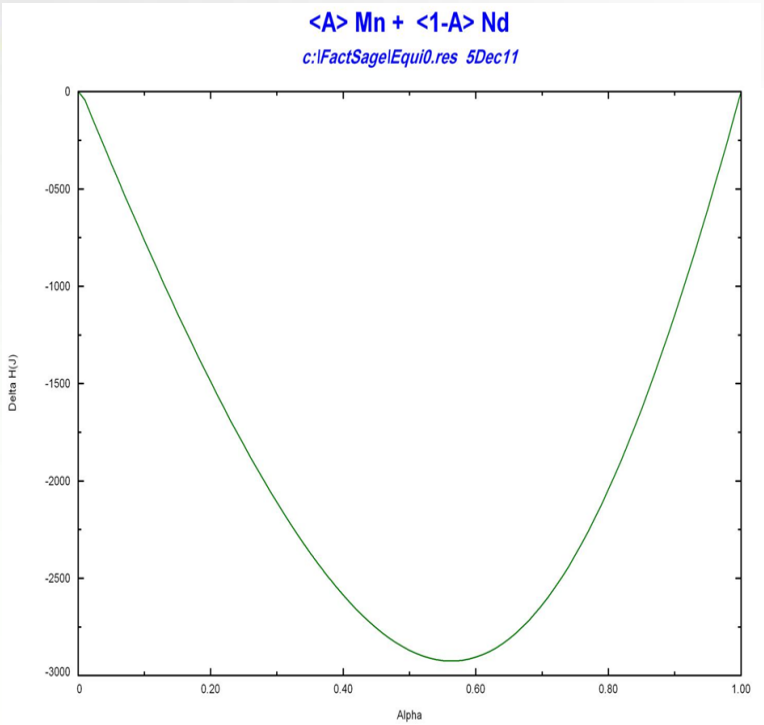
- Comparison between the experimental results and the thermodynamic model.



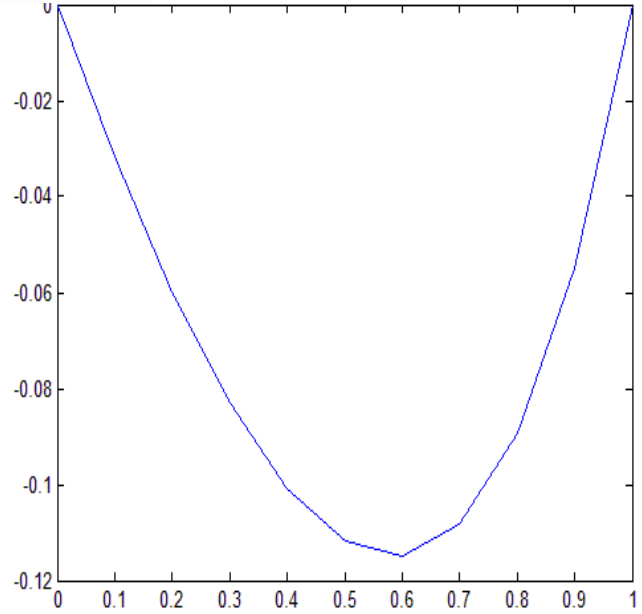


Mn-Nd Phase diagram

- Comparison between the Miedema`s value and the thermodynamic model of the heat of mixing for the liquid phase.



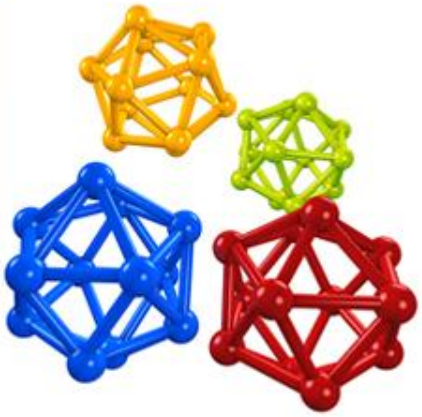
Calculated heat of mixing



Miedema`s heat of mixing

- Yet, the two curves are not corresponding. The parameters should be modified.

Conclusions



- **Success of optimization depends on:**
  - ✓ The selected model
  - ✓ The selected experimental data
  - ✓ The number of models parameters
  - ✓ Starting values for the model parameters
  - ✓ The order in which the parameters are arranged
- **Thermodynamic properties of the similar systems are the easiest way to start with.**
- **Many improvements are required to justify the Mn-Nd phase diagram model**
- **The final model can be used in extrapolating the Mg-Mn-Nd ternary phase diagram.**

Thank you