Thermodynamic Modeling
Mn-Nd phase diagram

By
Ahmad Mostafa

Presented to
Dr. Mamoun Medraj
• 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
The critical evaluation of the collected data by discarding the bad or contradictory data, using the following methods:

Second step

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

Recording the data

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

• This can reduce the number of phases that may be optimized together

Stable and metastable phases of Al-Mg phase diagram

H. Kumar, and P. Wollants, 2001
• 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:

- $\Delta H_{\text{formation}}$ of transition metal compounds can be obtained by *Miedema`s method*
- $C_p$ (Molar) can be approximated by *Kopp-Neumann rule*
- Excess partial molar Gibbs energies can be calculated by $x_sG_A = RT \ln \gamma_A$ and $x_sG_B = RT \ln \gamma_B$
- Experimental slopes of the phase boundaries involving the terminal phases in binary systems can be checked by *Van’t Hoff`s equation*
• Application of Van’t Hoff’s equation

\[ \left( \frac{dX}{dT} \right)_{\text{solidus}} - \left( \frac{dX}{dT} \right)_{\text{liquidus}} = \frac{\Delta H_{\text{fus}}}{RT_m^2} \]

\( X \): is the mole fraction of the solute

\( \Delta H_{\text{fus}} \): Enthalpy of fusion

\( T_m \): melting point of the pure element

The initial value of \( \left( \frac{dX}{dT} \right)_{\text{solidus}} \) for the terminal phases = 0, then:

\[ \Delta H_{\text{fus(Nd)}} = -\left( \frac{dX}{dT} \right)_{\text{liq(Nd)}} \times RT_m^2 \]
ii. Data of similar systems can also offer a great deal of information

Mn-Pr phase diagram from literature

Mn-Nd phase diagram recently studied

Saccone et al., 1985
Gibbs energy models

\[ G = G^{\text{ref}} + G^{\text{ideal}} + G^{\text{xs}} + G^{\text{phys}} \]

- **G\text{ref}**: Reference surface for Gibbs energy
- **G\text{ideal}**: Gibbs energy for ideal mixing
- **G\text{xs}**: is the excess Gibbs free energy
- **G\text{phys}**: physical contribution energy

❖ **Types of thermodynamic models:**

- Regular Solutions Models
- Sublattice Model
- Associated Solutions
- Cluster Variation Model
- Quasi-chemical Model
- Cluster Expansion Model
• 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.
• The Gibbs energy for the terminal solid solution phases is described by the following equation

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

\( \phi \): 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

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

\[
L_{i,j}^\phi = a_n + b_n \times T
\]

- Where, \( a \) and \( b \): are the parameters of the model need to be optimized.
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.
• From similarity with Mn-Gd system, the parameters (Jmol⁻¹) can be concluded:

\[ \begin{align*}
L(\text{LIQUID,Gd,Mn;0}) &= -5020.871 + 0.56166 \times T \\
L(\text{LIQUID,Gd,Mn;1}) &= 1041.42 \\
G(\text{Mn}_{12}\text{Gd},\text{Mn:Gd;0}) &= -52000 + 12.1 \times T + 12 \times G_{\text{Mn}} + G_{\text{Gd}} \\
G(\text{Mn}_{23}\text{Gd}_6,\text{Mn:Gd;0}) &= -185000 + 27.6 \times T + 23 \times G_{\text{Mn}} + 6 \times G_{\text{Gd}} \\
G(\text{Mn}_2\text{Gd},\text{Mn:Gd;0}) &= -19242 + 2.87 \times T + 2 \times G_{\text{Mn}} + G_{\text{Gd}} \\
G(\text{FCC A1,Gd;0}) &= 10000 + G_{\text{Gd}} \\
L(\text{BCC A2,Gd,Mn;0}) &= 50000 \\
L(\text{HCP A3,Gd,Mn;0}) &= 50000 \\
L(\text{FCC A1,Gd,Mn;0}) &= 50000
\end{align*} \]
• Applying the obtained parameters for Mn-Nd phase diagram optimization:
• Comparison between the experimental results and the thermodynamic model.
• Comparison between the Miedema`s value and the thermodynamic model of the heat of mixing for the liquid phase.

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