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Thermodynamic modelling of high temperature systems

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- Gibbs Energy Minimisation
- Thermodynamic Modelling Development
- Thermochemical Packages
- Application
Introduction

- Thermodynamic modelling?
  - 2nd law thermodynamic:
    predict composition at equilibrium

- Purpose of thermodynamic modelling:
  - Predict chemical composition
  - Constructing phase diagram
  - Tool for process development

Bale et al, 2008

Brooks et al, 2006

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Gibbs Energy Minimisation

- Based on Second Law Thermodynamics

\[ G = \sum_{i=1}^{p} n_i G_i^\phi = \text{total free energy system} = \text{minimum}; \]

\[ \sum_{i=1}^{p} n_i a_{ji} = b_j; \text{mass balance constraint} \]

- Gibbs energy for real solution:

\[ G^\phi = G^o + G^{\text{ideal}} + G^{\text{ex}} \]

\[ G^{\text{ideal}} = RT \sum x_i \ln x_i \]

\[ G^{\text{ex}} = RT \sum x_i \ln \gamma_i \]

- \( \gamma_i \), activity coefficient = f(x,T)
Development of Thermodynamic Modelling

1. Define System, Phase, Species
2. Define Database
3. Initial Species, Quantities, Operating Condition
4. Solution Models, Activity Coefficient
5. Equilibrium Calculation

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Database

- Thermodynamic data: Enthalpy (H), Entropy (S), Heat Capacity (Cp), activity coefficient (γ)
  - Data taken from calorimetric measurement, Differential Thermal Analysis (DTA)
  - Activity coefficient data can be taken from Electromotive Force (EMF), Knudsen Cell, vapor pressure measurement

- Experimental data are assessed and modelled as function of temperature
  - \( G = a + bT + cT\ln T + \Sigma dT^n \)
  - \( H = a -cT - \Sigma (n-1)dT^n \)

- Example of database: SGTE (Scientific Group Thermodata Europe), FACT (Facility on Analysis of Chemical Thermodynamic)
Solution Models

In high temperature systems, it is common for species to dissolve and form multi-component phases: e.g. slags, matte, alloys

Solution models have been developed to describe interactions in solutions

Some of example of solution model:

1. Ideal Solution Model
   - No interaction between molecules, $a = x$
   - Starting points to calculate thermodynamic modelling
Solution Models (continue)

2. Dilute Solution Model
   - Henry’s law: \( a = \gamma_i x_i \)
   - \( \gamma_i \): Henrian activity coefficient

3. Regular Solution Model
   - Interaction parameter independent of \( P \) and \( T \)
     \[
     ex \ G^\phi = x_i x_j L
     \]

4. Random Mixing Solution Model
   - For disorder substitutional solution
   - Interaction between species is called excess term
     - Redlich-Kister equation:
       \[
       ex \ G^\phi = x_i x_j \sum_{n=0}^{n=m} L_{i,j}^\phi (x_i - x_j)^n
       \]
5. Compound Energy Formalism (Hillert, 2001)

- For crystalline that have 2 or more lattice structures.
- Can describe thermodynamic properties with interstitial and vacancy
- Basic formula:

\[
G^{xs} = y_i y_j \sum_{k=0}^{n} L_{ij}^S (y_i - y_j)^k \quad y_i^s = \frac{n_i^s}{N^s} \quad x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{va}^s)}
\]


- For short-range ordering solutions: molten slags, matte
- Formula:

\[
G^{\text{liq}} = n_i^o G_i^{\text{liq}} + n_j^o G_j^{\text{liq}} - T \Delta S_c + \frac{n_{ij}}{2} G^{\text{ex,liq}}
\]

- \( \Delta G_{ij} \) is noted as \(( \omega - \eta T )\)
Thermochemical Packages

Chemix (CSIRO-SGTE Thermodata System)

FactSage (ThermFact Canada)

HSC Chemistry (Outokumpu Finland)

MTDATA (NPL UK)
# Comparison between Thermochemical Packages

<table>
<thead>
<tr>
<th>Packages</th>
<th>Chemix</th>
<th>HSC</th>
<th>FactSage 6.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Database</td>
<td>SGTE, JANAF, NPL</td>
<td>Barin, JANAF</td>
<td>SGTE 2009, FACT 2009</td>
</tr>
<tr>
<td>Solution Models</td>
<td>Fixed, Polynomial, Debye-Huckel, Interpolation, Virial, Bethelot, Subregular, Redlich, Margules, Redlich-Kister, Lupis-Elliot, Virial Full, Pitzer, Redlich-Kister, Regular</td>
<td>-</td>
<td>Quasichemical, Sublattice, Pitzer, Polynomial (Muggianu), Polynomial (Kohler/Toop), CEF</td>
</tr>
<tr>
<td>Modules</td>
<td>Reaction, Equilibrium</td>
<td>Reaction, Equilibrium</td>
<td>Equilibrium, Phase Diagram, optimisation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Equilibrium, Phase Diagram, optimisation, solidification</td>
</tr>
<tr>
<td>Application</td>
<td>-</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>interface</td>
<td></td>
<td></td>
<td>Yes (Matlab, Comsol)</td>
</tr>
<tr>
<td>Own solution</td>
<td>Possible</td>
<td>-</td>
<td>Possible</td>
</tr>
<tr>
<td>data</td>
<td></td>
<td></td>
<td>Possible</td>
</tr>
</tbody>
</table>

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Magnesium oxide is reduced by ferrosilicon to produce Mg vapour at 1160 °C and 7 Pa

Reaction: \(2 \text{CaO.MgO + FeSi = 2 Mg} \_{(g)} + \text{Ca}_2\text{SiO}_4 + \text{Fe}\)

Magnesium vapor condensed in condenser
Phases and Solution Models in the Pidgeon Process

<table>
<thead>
<tr>
<th>Phase</th>
<th>Solution Model</th>
<th>$\gamma$, activity Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase: (Mg, Ca, SiO, Fe, Al)</td>
<td>Ideal Solution</td>
<td>$\gamma = 1$</td>
</tr>
<tr>
<td>Monoxide Phase: (CaO, MgO, FeO, SiO$_2$)</td>
<td>Regular solution for MgO-FeO system</td>
<td>$\ln \gamma_i = L$</td>
</tr>
<tr>
<td></td>
<td>Sub-regular for CaO-MgO system</td>
<td></td>
</tr>
<tr>
<td>Dicalcium silicate: (Ca$_2$SiO$_4$, Mg$_2$SiO$_4$)</td>
<td>Random mixing Solution model for Ca$_2$SiO$_4$ and Mg$_2$SiO$_4$</td>
<td>$\sum_{n=0}^{\infty} L_{i,j} \left(x_i - x_j\right)^n$</td>
</tr>
<tr>
<td>Metal Phase: (Mg; Ca, Al, Fe, Si impurities)</td>
<td>First Assumption: Ideal Solution</td>
<td>$\sum_{n=0}^{\infty} L_{i,j} \left(x_i - x_j\right)^n$</td>
</tr>
<tr>
<td></td>
<td>Second assumption: Random mixing solution model for fcc, bcc, and hcp solid solution.</td>
<td></td>
</tr>
</tbody>
</table>

There are formation of solid impurities at temperature range between reaction zone and condenser zone.

- Ideal Solution: 98.33%
- Random Mixing Solution: 99.98%
Conclusion

- Thermodynamic modeling is a valuable tool to predict phase equilibria in high temperature metals processing.
- Thermochemical packages make modeling easier, but the fundamental knowledge such as how we determine the phase, species, and activity behaviour are the intellectual aspects.
- An example in magnesium impurities illustrate both the predictive power of thermodynamic modelling and the dilemmas associated with solution behaviour.
Thank You